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PHOTOCHEMISTRY
and the
Mechanism of Chemical Reactions

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'PHOTOCHEMISTRY
and the
Mechanism of Chemical Reactions

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PREFACE

ALTHOUGH we have endeavored to present this discussion of photochemistry in such a way that the reader with but a limited knowledge of the subject may understand its background and realize its possibilities, it is our intention that the specialist may use the work to acquaint himself quickly with the progress made in associated problems. In an effort to be critical and in the interest of economy (of the reader's time), we have deliberately selected data which represent what is believed to be the present status of the specific problems considered. The reader will find that the latest papers are rather thoroughly surveyed; in those cases where a thorough resume of publications has not been attempted, the most recent references provide a key to the complete literature.

We have consistently endeavored to maintain a critical attitude. The data are not always presented with the point of view of the original authors. When such departures have been made, they have been indicated. When doubt has been felt, it has been expressed. Throughout the book there have been emphasized not only the questions which photochemistry has answered but also the questions to which it must still provide an answer.

The first five chapters are devoted to a presentation of the fundamental concepts required for an understanding of the effects produced by the absorption of light and the behavior of the reactive states produced in this manner. It has been borne in mind in writing these chapters that complete knowledge of spectroscopy, atomic structure, and quantum mechanics is *not* essential for an understanding of photochemistry. For example, the discussion of spectra is by no means complete. However, it is only in rare cases that the reader will require any more detailed information than is presented in this book. We have tried to stress ideas rather than to dazzle the reader with complicated equations. Indeed, we maintain that it is possible for a person to use this book without resort to any more specialized works and at the end to find himself with a working understanding of what has been done and an appreciation of what is still needed.

The last ten chapters deal with specific reactions. It is not suggested that these chapters should necessarily be read in order. For example, portions of Chapters IX and X are supplementary to Chapter III; portions of Chapters VII, VIII, and IX may be read with Chapter IV; portions of Chapters XI, XII, and XIII with Chapter V. Chapters VI and XIV are worthy of perusal for their own sake. The content of Chapter XV should be deferred until the more elementary concepts are well established in the mind of the reader; it serves principally to indicate what can be done with more complex systems.

We have the pleasant duty of expressing our gratitude to several of our colleagues who have assisted in the compilation of data and have offered helpful suggestions in regard both to form and subject matter. Among these are included Dr. J. E. Booher, of San Francisco Junior College; and Dr. M. Calvin, Professors W. F. Libby, A. R. Olson, and C. W. Porter, and Dr. S. Ruben, all of the University of California. We wish also to thank Mr. A. R. King for the preparation of the figures used in the book. Finally, we desire to express our appreciation to Professor James Franck, of the University of Chicago, who initiated the chain of circumstances which led to the writing of this book.

GERHARD K. ROLLEFSON

MILTON BURTON

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION	1
History. Grotthus and Draper. Law of photochemical equivalence. Influence of quantum theory. Free atoms and radicals. Sequence of subjects considered.	
II. THE QUANTUM THEORY OF SPECTRA	6
Some fundamental ideas: quantization of energy; Bohr's fundamental postulates. Description of energy levels: empirical laws for series in spectra; assignment of quantum numbers to terms; notation; designation of spectrum lines; multiplicity and the periodic table; effect of a magnetic field. Molecular spectra: pure rotation spectra; vibration-rotation spectra; electronic bands; multiplicity in molecular spectra. Vibrational structure of electronic bands. Potential energy curves: Morse curves for the potential energy of molecules. The uncertainty principle.	
III. PHOTOACTIVATION AND THE PROPERTIES OF PHOTOACTIVATED MOLECULES: I. PHYSICAL EFFECTS . . .	34
Photoactivation: laws of absorption. Reactions of the photoactivated molecule: mean life of an activated molecule; correlation of absorption coefficient and transition probability; life periods of activated molecules. Fluorescence: quenching of fluorescence; resonance of sodium vapor; mercury fluorescence; fluorescence of iodine vapor; quenching and energy transfers in other fluorescence spectra; conclusions from the study of fluorescence in gases. Fluorescence in the liquid state.	
IV. PHOTOACTIVATION AND THE PROPERTIES OF PHOTOACTIVATED MOLECULES: II. CHEMICAL EFFECTS . . .	59
Reactions of photoactivated molecules with other molecules. Photodissociation of molecules. Predissociation: selection rules for predissociation; predissociation in polyatomic molecules; effect of temperature; tests for predissociation. Predissociation in sulfur vapor. Predissociation in iodine vapor. Predissociation in formaldehyde vapor. Predissociation in sulfur dioxide. General conclusions. Dissociation processes for which only spectroscopic evidence has been obtained.	
V. REACTION KINETICS	89
Rate determining factors in photochemical reactions: efficiency of a photochemical reaction. Kinetic theory and rates of re-	

V. REACTION KINETICS (*Cont.*)

action: activation energy of a reaction; theoretical basis of activation energy. Experimental problems in reaction kinetics: determination of the overall rate law. Mechanisms for reactions. Kinetics of reactions involving atoms and radicals. Reactions of atoms and radicals with other molecules. Budde effect and Draper effect. Principle of microscopic reversibility. General considerations concerning the rate of the overall reaction and the selection of a mechanism; detection of free atoms and radicals.

VI. PHOTOLYSIS IN THE SOLID STATE 121

Order of discussion. Alkali halides in the solid state: a model for the photochemical act; normal absorption spectra of the alkali halides; production of F centers; production of F' centers; problems in the photolysis of alkali halides. Silver halides in the solid state: a model for the photochemistry of the silver halides; absorption spectra; quantum yield; problems in the photochemistry of silver halide crystals. Photolysis of some other crystal molecules. Effect of polarized light.

VII. PHOTOLYSIS OF VAPORS OF INORGANIC COMPOUNDS . . . 142

Classification. Ozone. Other oxides of the oxygen family: sulfur dioxide; sulfur trioxide. Oxides of nitrogen: nitrous oxide; nitric oxide; nitrogen dioxide and nitrogen tetroxide; nitrogen pentoxide; NO_2 ; nitrosyl chloride. Halogen oxides: oxides of fluorine; chlorine monoxide; chlorine dioxide; chlorine trioxide and chlorine hexoxide; chlorine heptoxide; bromine monoxide. Water; hydrogen peroxide; hydrogen sulfide; hydrogen selenide and hydrogen telluride. Ammonia; deuterio-ammonia; phosphine. Hydrogen halides: hydrogen iodide; hydrogen bromide. Alkane analogs: silanes; germane; diborane.

VIII. PHOTOLYSIS OF VAPORS OF CARBON COMPOUNDS . . . 196

Hydrocarbons: methane; ethane; other aliphatic hydrocarbons; benzene; diphenyl; other aromatic hydrocarbons. Alkyl halides. Amines; diazomethane; azomethane. Nitroalkanes and the alkyl nitrites and nitrates. Alcohols. Alkyl cyanides. General aspects of absorption spectra of aldehydes and ketones; special aspects of absorption spectra of the aldehydes; photochemistry of the aliphatic aldehydes; unsaturated aliphatic aldehydes; benzaldehyde; special aspects of absorption spectra of the ketones; photochemistry of the ketones. Fatty acids; esters; acetyl halides; acyl peroxides. Metallo-organic compounds.

IX. MOLECULAR REARRANGEMENTS 248

Types of intramolecular change. Rotation about a double bond: Olson's model; experimental evidence. Interchange of two atoms within a molecule. Shift within a molecule. Other reactions.

CHAPTER

PAGE

X. PHOTSENSITIZATION 266

Nature of photosensitization. Xenon-sensitized dissociation of hydrogen. Mercury-sensitized reactions: dissociation of hydrogen; reaction between hydrogen and oxygen; reaction between carbon monoxide and hydrogen; reaction between carbon dioxide and hydrogen; reaction between nitrous oxide and hydrogen; reaction between nitrogen and hydrogen. Mercury-sensitized decompositions: water; ammonia. Some other sensitized reactions; determination of activation energies; sensitized formation of ozone; sensitized decomposition of nitrogen pentoxide. Reactions photosensitized by the halogens: chlorine-sensitized decomposition of ozone; bromine-sensitized decomposition of ozone; bromine-sensitized rearrangement of maleic acid and its esters into the fumaric compounds; bromine-sensitized oxidation of CCl_3Br ; chlorine-sensitized decomposition of chlorine monoxide; sensitized decomposition of ClO_2 ; iodine-sensitized decomposition of ethylene iodide; iodine-sensitized rearrangement of allocinnamylidenacetic acid.

XI. TYPICAL CHAIN REACTIONS 296

Definition. Photosynthesis of hydrogen bromide; addition of thermal and photochemical rates. Photosynthesis of hydrogen chloride; reaction in pure hydrogen and chlorine; effect of impurities on the reaction between hydrogen and chlorine; effect of oxygen on the hydrogen-chlorine reaction: the chlorine-sensitized formation of water; effect of temperature and of wave length on the rate of formation of hydrogen chloride; formation of HCl in mixtures of ICl , H_2 , and Cl_2 . Photochemical formation of phosgene. Chlorination of methane and its derivatives; reaction between formaldehyde and chlorine; formic acid and chlorine; bromotrichloromethane and chlorine. Alkyl radicals and hydrogen atoms as chain carriers.

XII. ADDITION REACTIONS AND ASSOCIATED PHENOMENA. 325

Introduction. Photo-oxidation of acetaldehyde; photo-oxidation of benzaldehyde. Photochemical formation of ozone. Addition reactions involving the halogens: chlorination of ethylene; addition of chlorine and bromine to tetrachloroethylene; other reactions involving the addition of a halogen to an ethylenic linkage; addition of chlorine and bromine to acetylene; addition of the halogens to cyclic compounds.

XIII. POLYMERIZATION 341

Definition. Ethylene; acetylene. Anthracene. Phosphorus. Sulfur. Aldehydes.

CHAPTER	PAGE
XIV. EFFECTS IN THE LIQUID STATE.....	355
General effects: Franck-Rabinowitch hypothesis; aldehydes and ketones; other evidence concerning the Franck-Rabinowitch hypothesis; photohydrolysis of monochloroacetic acid; alkyl iodides; other examples of increased quantum yield in the liquid state. Specific solvent effects: halides in solution; hydriodic acid; alkali halide solutions. Other ions in solution: hydroxides; sulfur compounds; nitrates; bichromates and permanganates; cations. Photosensitization in solution. A case of inhibition: the decomposition of hydrogen peroxide. Oxidation and reduction. Some photochemical reactions involving oxalates. Effect of circularly polarized light.	
XV. HETEROGENEOUS REACTIONS.....	385
Importance of heterogeneous reactions. White pigments as sensitizers. Photography: quantum yield of the elementary photographic process; sensitivity of the grain; conditions of precipitation of the halide; sensitive dyes. Photosynthesis: its nature; products; locus; quantum yield; Blackman reaction; fluorescence; photosynthetic unit; a model for photosynthesis; photosynthetic studies with radio-carbon. Photosynthesis in vitro. Other heterogeneous photochemical reactions.	
APPENDIXES	
I. Comparison of Notations for Atomic Energy States...	417
II. Heats of Reaction and Bond Strengths.....	418
III. Energies of Activation.....	424
IV. Energy Conversion Chart.....	425
SUBJECT INDEX.....	429
AUTHOR INDEX.....	438

ILLUSTRATIONS

FIGURE	PAGE
1. Schematic representation of the H-atom spectrum	9
2. Grotrian diagram for sodium	11
3. Grotrian diagram for mercury	15
4. Magnetic splitting of yellow sodium doublet	17
5. Rotation-vibration spectrum for HCl	20
6. P_2 bands	21
7. Fortrat diagram	22
8. Transitions between vibrational levels	29
9. Potential energy diagram for S_2	31
10. Effective quenching cross section of various substances for Hg resonance radiation	49
11. Fluorescence excited by monochromatic radiation	50
12. Potential energy curves for the halogens	61
13. Energy relationships in absorption of a light quantum	62
14. Relative positions of potential energy curves in pre- dissociation	72
15. Potential energy diagram for I_2	82
16. Diagrammatic representation of the cross section of an alkali halide crystal	122
17. Hole in a crystal lattice	122
18. Absorption spectra of the alkali halide crystals	125
19. Quantum yields of the production of F' centers in KBr	130
20. Absorption curves for silver halides	135
21. Absorption curves for "discoloration" of silver halides	136
22. Quantum yields in the photolysis of silver halides	137
23. Extinction coefficient for ozone in the visible range	143
24. Extinction coefficient for ozone in the ultraviolet	144
25. Photographs of the absorption spectrum of ozone in the ultraviolet	145
26. Absorption spectrum of NO	155
27. Potential energy curves for the known states of NO	157
28. Predissociation spectrum of NO_2	160
29. Potential energy curves for NO_2	162
30. Extinction coefficients: (a) water vapor; (b) quartz	172
31. Extinction coefficients for hydrogen sulfide, hydrogen selenide, and hydrogen telluride	179
32. Quantum yields in the photolysis of NH_3	182

FIGURE	PAGE
33. Quantum yields in the photolysis of ND_3	186
34. Positions of the first bands of the alkenes.....	199
35. Diagrammatic representation of the absorption spectra of benzene and diphenyl below 2083 Å.....	200
36. Extinction coefficients for the alkyl halides.....	203
37. Absorption curves for diazomethane and azomethane.....	214
38. Absorption curves for some alkyl nitrites, alkyl nitrates, and nitroalkanes.....	218
39. Qualitative course of the extinction coefficient for methanol.....	219
40. Qualitative course of the extinction coefficient for methyl cyanide.....	221
41. Molecular extinction coefficients of aldehydes in hexane solution.....	222
42. Extinction coefficient of acetone in hexane solution.....	223
43. Extinction coefficients of the fatty acids.....	240
44. Potential energy of an ethylene molecule.....	250
45. Potential energy of $\text{RHC}=\text{CHR}$	251
46. Potential energy curves for normal and activated molecules.....	252
47. Variation of the <i>cis/trans</i> ratio with temperature, according to Olson's model.....	254
48. Potential energy curves for a normal molecule and for two activated states.....	255
49. A treatment of an unsymmetrical molecule.....	257
50. Potential energy diagram for the $\text{C}\equiv\text{C}$ link in acetylene.....	349
51. Absorption curve for the I^- ion in aqueous solution.....	369
52. Absorption curve for the Br^- ion in aqueous solution.....	369
53. Absorption curve for the Cl^- ion in aqueous solution.....	370
54. Extinction coefficient of sodium hydroxide in aqueous solution.....	373
55. Extinction coefficient of the nitrate ion in aqueous solution.....	375
56. Extinction coefficient of nitric acid at various dilutions in water and in ether.....	376
57. Absorption curves for the two chlorophylls.....	399
58. Fluorescence bands of the excited chlorophylls dissolved in ether.....	400
59. Energy conversion chart.....	425

TABLES

TABLE	PAGE
1. Values of J corresponding to various values of L and Σs	13
2. Multiplicities of the atoms by groups.....	16
3. Quenching of sodium resonance radiation by various gases at 200° C.....	43
4. Effective cross sections and vibration bands for molecules which quench mercury fluorescence.....	45
5. Comparison of thermal and spectroscopic values for heats of dissociation of the halogens.....	64
6. Photodissociation processes and the effective wave lengths.....	87
7. Quantum yields of typical photochemical reactions....	91
8. Rate constant for $\text{Br} + \text{Br} + \text{M} \rightarrow \text{Br}_2 + \text{M}$	104
9. Positions and comparisons of the absorption maxima of the solid alkali halides.....	127
10. Photochemical studies of some solid substances.....	140
11. Quantum yields in the photolysis of NO_2 and N_2O_4	163
12. Data on absorption spectra of simple alkyl halides....	204
13. Near-ultraviolet absorption spectra of the vapors of the aldehydes.....	224
14. Near-ultraviolet absorption spectra of the vapors of the ketones.....	233
15. Estimate of the per cent decomposition into free radicals in the photolysis of several ketones.....	237
16. Absorption coefficients of the acetyl halides.....	244
17. Photochemistry of the metallo-organic compounds....	246
18. Quantum efficiencies of isomerizations.....	259
19. Quantum efficiencies of isomerization of the nitrobenzaldehydes.....	262
20. Some photosensitized decompositions.....	285
21. Bromine-sensitized photochemical reactions of maleic acid and its esters.....	290
22. Data on polymerization of some ethylene and acetylene derivatives, etc.....	347
23. Quantum yields of some reactions in gaseous and condensed systems.....	362

TABLE	PAGE
24. Quantum yields of the photolysis of some alkyl iodides, etc., in the liquid state and in solution.....	365
25. Quantum yields of two reactions favored in the condensed state and by decreasing wave length.....	366
26. Quantum yield of photolysis of hydrogen iodide in water.....	371
27. Absorption thresholds of white pigments.....	387
28. Quantum yield of the elementary photographic process..	392
29. Dictionary of notations for atomic states.....	417
30. Heats of dissociation of several diatomic elements.....	419
31. Heats of formation of compounds.....	420
32. Bond strengths in organic compounds.....	422
33. Activation energies of some simple reactions.....	424

PHOTOCHEMISTRY
and the
Mechanism of Chemical Reactions

CHAPTER I

INTRODUCTION

1.1 History. The fact that light plays an important part in certain chemical processes such as the growth of plants or the bleaching of dyes has been known since ancient times. However, it is only recently that such processes have been studied extensively. Probably the first work which can be considered as photochemistry is that of Stephen Hales (1677-1721) on photosynthesis. The sensitivity of the silver salts to light was established during the eighteenth century by the work of Schultz (1727) on silver carbonate and by that of Beccarius (1757) and Scheele (1777) on silver chloride. Scheele showed that the sensitivity of the silver chloride varied with the wave length, increasing toward the violet. About the end of the eighteenth century and in the first few years of the nineteenth, other reactions were found to be photosensitive. Among these were several involving chlorine, particularly the formation of hydrogen chloride from the elements, the union of CO and Cl_2 , the chlorination of methane, and the decomposition of chlorine water.

1.2 Grotthus and Draper. In this early work the substances under investigation were exposed either to sunlight or to some convenient source of artificial light, but no general relationship between the nature of the light used and its efficiency in causing reaction was recognized until 1817. In that year Grotthus stated what is usually called the first law of photochemistry; namely, only the light that is absorbed by a system can cause a chemical reaction to occur in it. This is a purely qualitative law, since light may be absorbed without causing any net chemical reaction. The first quantitative correlation of the amount of reaction with the intensity of the absorbed light appeared in the work of Draper (1841) on the hydrogen-chlorine reaction. He found

that after the initial induction period the rate of the reaction was proportional to the intensity of the light used. Many other reactions in which the rates were proportional to the light intensity were discovered in the latter part of the nineteenth century. Other reactions were found in which the rate depended on the light intensity but according to some less simple law. At the beginning of the twentieth century it was recognized as a result of these studies that, in order to cause chemical reaction, light has to be absorbed and that there is a correlation between the amount of reaction and the amount of light absorbed in the effective region of the spectrum.

During this period light was looked upon essentially as a reagent which could cause certain reactions that would otherwise require much higher temperatures for their occurrence. After Arrhenius (1887) put forth his ideas concerning the "activation energies" required by molecules in order to react, many photochemists considered that the action of light was to supply some of this activation energy. Such considerations did not lead to any great advances in photochemistry, since, for reasons which will be presented in this book, there is no simple correlation between the light absorbed in a photochemical reaction and the activation energy of the corresponding thermal reaction. The change from this point of view to the present day one, in which photochemistry is looked upon as a tool for the study of the detailed mechanisms of reactions, was brought about by the development of the quantum theory.

1.3 Law of photochemical equivalence. Although Planck introduced the idea of units of radiant energy of the magnitude $h\nu$ in his treatment of the theory of heat radiation presented in 1900, some years elapsed before this idea was applied to photochemical reactions. Then Stark,¹ and later Einstein,² introduced the idea that one quantum ($h\nu$) of

¹ Stark, (a) *Physik. Z.*, **9**, 889, 894 (1908); (b) *Prinzipien der Atom-Dynamik*, S. Hirzel, Leipzig, 1911, vol. II, p. 207; (c) *Ann. Physik*, **38**, 467 (1912).

² Einstein, *Ann. Physik*, **37**, 832 (1912); **38**, 881 (1912); *J. phys.*, **3**, 277 (1913).

active light is absorbed per molecule of absorbing and reacting substance which disappears. This law was originally deduced for extremely simple reactions of the first order, and it was Stark^{1c} who first emphasized that in a strict sense it applied only to the primary process and that various secondary processes might introduce many complications. The first extensive discussions of this law with reference to experimental data appear to be those by Bodenstein and by Warburg. Bodenstein³ estimated *quantum yields* (molecules reacting/quanta absorbed) for twenty-two reactions and found values ranging from 0.002 for the bleaching of certain dyes to 10^6 for the combination of hydrogen and chlorine and the bromination of toluene. Warburg⁴ at the same time began a series of experimental studies using the decompositions of NH_3 and O_3 as his first two examples. These investigations, and others which followed soon after, demonstrated very clearly that the secondary processes following the primary action of the light were of great importance. The study of photochemistry therefore developed along two lines: (1) the determination of the nature of the primary process; (2) the study of the secondary processes.

1.4 Influence of quantum theory. A second factor which contributed to the rapid development of photochemistry at this time was the application of quantum theory to spectra. In 1913 Bohr, in connection with his theory of atomic structure, advanced the idea that the frequency of light absorbed or emitted by an atom or molecule is determined solely by the energies of the initial and final states of the system. Applying this principle to photochemical reactions, it can be said that the activating influence of the light consists of transferring the molecule from its normal non-reactive state to a state of higher energy in which it is more reactive. Thus, if light of a particular frequency is absorbed, the

³ Bodenstein, *Z. physik. Chem.*, **85**, 329 (1913).

⁴ Warburg, *Sitz. kgl. preuss. Akad.*, 746 (1911); 644 (1913). See also a summary in *Z. Elektrochem.*, **26**, 54 (1920).

molecule is put into one definite reactive state. If this state is known, photochemistry is a powerful tool for the study of the reaction mechanism involved.

In the first years there was much argument as to whether the molecules were dissociated by the light or merely put into a higher energy level. The great single step in the clarification of this situation was the work of Franck,⁵ in which he correlated the convergence limits of the visible bands of the halogens with their dissociation energies. A few years later the so-called "predissociation spectra" were explained on a similar basis. The development of these discoveries has led to the correlation of certain types of absorption spectra with dissociation, and other types with the formation of activated molecules. Some other cases exist in which the absorption of light puts the molecule into a higher state in which it exists for a long time compared with the period of vibration. Under such conditions it is sometimes necessary to carry out rather extensive experiments in order to establish definitely the nature of the molecule that enters into any secondary processes. Many methods will be discussed in detail in the later chapters of this text.

1.5 Free atoms and radicals. Paralleling the developments in the field of spectroscopy have been discoveries concerning the behavior of atoms and free radicals. In this field we have the work with atoms or radicals produced by the action of an electric discharge, as illustrated by the work of Wood⁶ and of Bonhoeffer.⁷ Atoms of hydrogen have also been produced by collisions of molecules with excited mercury atoms.⁸ Many simple organic radicals are produced in thermal reactions, and special methods have been devised for studying their properties. An excellent review of this work has been prepared by F. O. Rice and K. K. Rice.⁹

⁵ Franck, *Trans. Faraday Soc.*, **21**, 536 (1926).

⁶ Wood, *Phil. Mag.*, **42**, 729 (1921); **44**, 538 (1922).

⁷ Bonhoeffer, *Z. physik. Chem.*, **113**, 199 (1924); *Ergeb. exakt. Naturw.*, **204** (1927).

⁸ Cario and Franck, *Z. Physik*, **11**, 161 (1922); **36**, 61 (1926).

⁹ F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals*, Johns Hopkins Press, Baltimore, 1935.

These developments were of particular importance in photochemistry; they assisted in the determination of the product formed in the primary process, and of the secondary reactions which follow the primary action of the light.

1.6 Sequence of subjects considered. In general, photochemical reactions are rather complex. Therefore, prior to a discussion of particular reactions, the next chapters are devoted to a presentation of the basic principles involved. As the first step, the quantum theory is considered as applied in the theory of spectra. Then there is discussed the interaction of light with atoms and molecules, and the properties of the activated states produced. This is followed by a brief review of the basic principles of chemical kinetics. The remainder of the book is devoted to detailed experimental and theoretical consideration of the principal subjects in the study of which photochemistry has proved a valuable tool.

CHAPTER II

THE QUANTUM THEORY OF SPECTRA

2.1 Some fundamental ideas. The subject matter concerning atomic and molecular spectra may be divided into two classes: first, a large amount of experimental data which has been collected and tabulated empirically during the last half century; second, the theories and models which have been devised to explain the experimental facts. The models are not to be looked upon as realities. They represent merely an attempt to relate ordered but unexplained data to simple concepts with which we are already familiar. It is necessary therefore to proceed with caution in applying a model to data other than those for which it was designed. Also, it must be remembered that arguments which may invalidate a model do not affect the validity of the experimental facts on which that model was based. Usually the complexity of a model depends on the complexity of the data which are to be explained. In this chapter we shall make use of models in the discussion of the quantum numbers used to describe atomic and molecular energy states. It must be remembered, however, that the validity of these quantum numbers is in no way affected by the validity or non-validity of the atomic and molecular models. Such a set of numbers could be set up as a purely empirical device for the description of the states.

2.11 Quantization of energy. The most fundamental concept required in the discussion of spectra is that the energy of a system varies by units, known as *quanta*, which bear the same relationship to the quantities of energy we usually measure as molecules do to the quantities of material ordinarily handled. This idea was first applied to emission processes by Planck,¹ but he apparently did not consider

¹ Planck, *Verhandl. deut. physik. Ges.*, **2**, 202 (1900).

that light itself was made up of such units. The latter idea was introduced by Einstein² to explain the photoelectric effect. The experimental facts to be explained are: (1) for a given wave length of light, the number of photoelectrons emitted is directly proportional to the intensity of the incident light; (2) the kinetic energy of the photoelectrons is directly proportional to the frequency of the incident light. These observations are in accord with the assumption that a single electron absorbs the entire energy of a light quantum and thereby acquires a kinetic energy equal to $h\nu$. Some of this energy is required to bring the electron out of the substance, leaving a kinetic energy for the escaping electron of

$$\frac{1}{2}mv^2 = h\nu - h\nu_0 \quad 2-1$$

The frequency ν_0 is found experimentally by determining the *photoelectric threshold*; i.e., the minimum frequency which will produce a photoelectric effect with a given substance.

2.12 Bohr's fundamental postulates. The correlation of the concept of light quanta with the changes of energy which occur in atoms and molecules is supplied by the two fundamental postulates stated by Bohr.³ They are:

I. The energy of an isolated atom does not vary continuously but assumes only such values as are characteristic of stationary states which exist within the atom.

II. The frequency of the radiation associated with a change from one stationary state to another is given by the relation

$$\nu = \frac{E_2 - E_1}{h} \quad 2-2$$

in which E_2 is the energy of the final state and E_1 that of the initial state of the atom.

Although these postulates were originally stated for atoms, they apply equally well to molecules. It is to be noted that these postulates do not presuppose any particular

² Einstein, *Ann. Physik*, **17**, 132 (1905).

³ Bohr, *Phil. Mag.*, **26**, 1, 476, 857 (1913).

theory of atomic or molecular structure. Any model may be used provided it is compatible with the assumption of the existence of stationary states or, as we shall call them, *energy levels* in the system. At times it is convenient to use a mechanical model, but care must be taken not to draw too rigid conclusions on the basis of any assumed structure.

2.2 Description of energy levels. The energy levels of an atom are described by means of four quantum numbers, n , L , J , M . In the absence of an external field, n , L , and J are sufficient. These numbers⁴ may be given certain physical significance in terms of atomic models, but the validity of their use in the description of the atomic states and of the rules governing the permitted changes in their value on the emission or absorption of light is not affected by the validity of the assumed model. If we assume a model which consists of a positive nucleus with electrons moving about it, then L may be thought of as representing the resultant of the angular momentum of the electrons about the nucleus; J , the total angular momentum of the atom obtained by vectorial summation of the orbital momenta of the electrons and the spins of the electrons; and M , the component of J in the direction of an external field. The number n is used to distinguish between states which have the same L value, and it increases as the energy of those states increases.

2.21 Empirical laws for series in spectra. From an experimental standpoint our best evidence for the existence of discrete energy states within the atom is obtained from line spectra. The first observation of a regularity in a line spectrum was made by Balmer in 1885. He found that the hydrogen spectrum contains a group of lines the frequencies of which can be represented by the formula

$$\nu = R \left(\frac{1}{4} - \frac{1}{n^2} \right)$$

⁴ We are disregarding a fifth number which is required for the hyperfine structure of the lines in atomic structure. Furthermore, in this discussion we shall restrict ourselves to those systems which obey the Russell-Saunders coupling. The other systems are of no importance in photochemistry. For a more complete discussion, see Herzberg, *Atomic Spectra and Atomic Structure*, Prentice-Hall Inc., New York, 1937.

in which n can be 3, 4, 5, 6, etc. Later Lyman, Paschen, and Brackett found other series for which the first terms are 1, $1/9$, and $1/16$ respectively. We can represent all of these series by the equation

$$\nu = R \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \quad 2-3^5$$

where n_1 and n_2 are positive integral numbers and n_1 must be at least $n_2 + 1$. Fig. 1 shows diagrammatically the positions of the various series in the hydrogen spectrum. This equation also requires that the difference in frequency between the first and second lines of the Lyman series be equal to the frequency of the first line of the Balmer series, and that the difference between the second and third lines be the same as the first line of the Paschen series. Such a conclusion is in agreement with the experimental facts, and led Ritz to the statement known as the *combination principle*, which says: the frequency of any line in a spectrum which has been resolved into series can be expressed as a difference of two terms and, with certain exceptions, the difference between any two such terms is the frequency of an observed line.

Balmer's discovery served as a great stimulus to the study of line spectra and, in the years that followed, many series were discovered in the emission spectra of other elements by Rydberg and by Kayser and Runge.

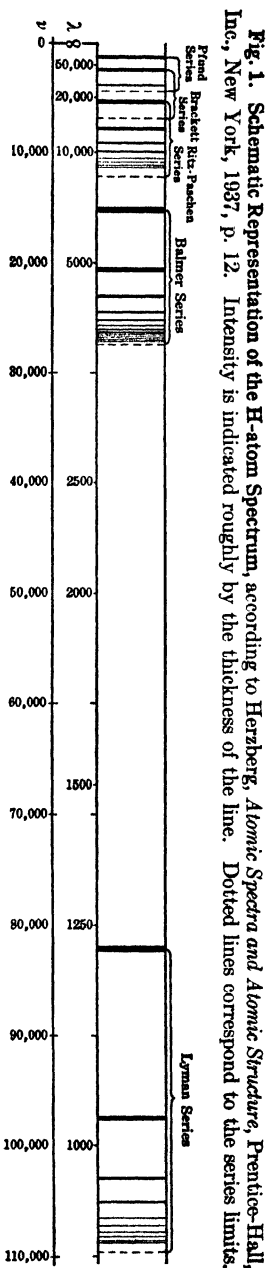


Fig. 1. Schematic Representation of the H-atom Spectrum, according to Herzberg, *Atomic Spectra and Atomic Structure*, Prentice-Hall, Inc., New York, 1937, p. 12. Intensity is indicated roughly by the thickness of the line. Dotted lines correspond to the series limits.

⁵ This formula is not concerned with the fine structure of the lines.

Although various formulas have been devised to express the frequencies of the lines in a series, the only one we need to consider is Rydberg's, which has the form

$$\nu = A - \frac{B}{(n + \sigma)^2} \quad 2-4$$

where A , B , and σ are constants for a given series and n is a positive integer. The constant B either is equal to the Rydberg constant R , which appears in the equation for the series for hydrogen, or is 4, 9, or 16, etc. times that value.⁶ Series of this type were found in all of the simpler spectra, especially those of the alkali atoms, alkaline earths, and the corresponding sub-groups in the Periodic Table. From the study of such spectra, series of characteristic *term values*⁷ were built up for a number of elements, and these terms were designated empirically as S , P , D , etc. The so-called fine structure of these terms was taken into account by designating the subdivisions by subscripts such as P_1 , P_2 , P_3 .

A typical set of these term values, as found for sodium, is shown graphically in Fig. 2. This figure also shows the observed transitions and brings out the fact that not all combinations of terms lead to spectrum lines. In the diagram all the S terms are single, and the P and D terms double. This type of spectrum is found for all elements which have only one valence electron, such as sodium, potassium, silver, etc. Elements with two valence electrons, such as calcium, magnesium, etc., are found to have two sets of single S terms and two sets of P , D , etc. terms, one of which is made up of single terms and the other of triplets. Furthermore, it has been found, if we arrange the terms as S , P , D , F , etc., that S terms combine only with P terms either in emission or absorption; P terms combine only with S and D terms; D terms, only with P and F . It

⁶ Actually the constant R varies slightly with the atomic weight according to the equation $R_\infty/R_m = 1 + m_e/m$ in which m_e is the mass of the electron and m the mass of the nucleus. The range of values is shown by the following examples: $R_H = 109,677$, $R_{He} = 109,722$, $R_\infty = 109,737$. It is obvious that for most elements we may use R_∞ .

⁷ The expressions *term* and *term values* were introduced by spectroscopists who found it convenient to tabulate the values of the two terms on the right-hand side of equation 2-4 instead of the lines which were defined by those terms.

is such empirical facts which have now been interpreted in terms of the quantum theory.

2.22 Assignment of quantum numbers to terms. We shall not undertake to present the modern quantum theory of atomic spectra from the historical standpoint. Our present picture is that all the term values found in spectroscopy correspond to the energies of stationary states

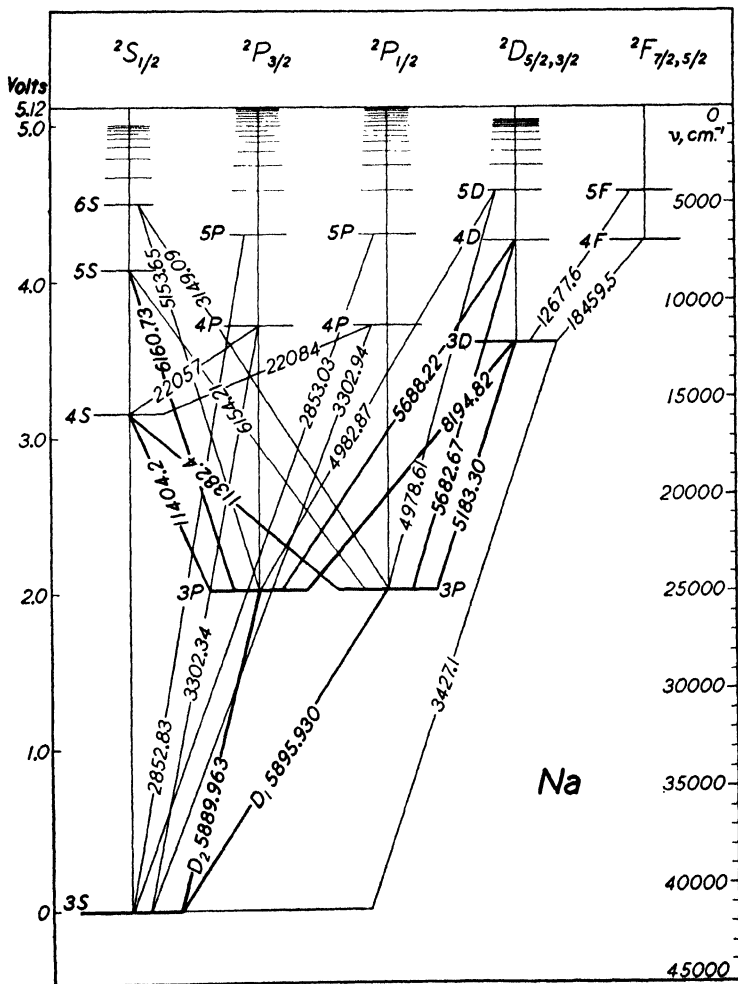


Fig. 2. Grotrian Diagram for Sodium.

such as were postulated by Bohr. The various S terms represent states of different quantum number n but all having the same value of the quantum number L . The P terms, similarly, have different values for n but the same L , which, however, is different from that of the S terms. The values of L for the different terms are as follows:

TERM.....	S	P	D	F	G	H	I
L	0	1	2	3	4	5	6

The observed combinations are governed by the selection rule $\Delta L = \pm 1$.

The subdivisions of the S , P , D , etc. terms are determined by the third quantum number J . It was found empirically that the J values required for elements in the odd-numbered groups of the Periodic Table are an odd number times one-half, i.e., $1/2$, $3/2$, $5/2$. In the even-numbered groups, all the J values are integral. Furthermore, if a is the number of valence electrons in the atom, J may be considered to be the vector sum of L and $a \times \frac{1}{2}$, or the sum of L and any combinations of a units of $1/2$ which differ from each other by a small integral number. This half unit for each electron has been associated with a model in which the electron is spinning with an angular momentum which may be represented by $1/2$. For a electrons these half units may be added vectorially to give a maximum value of $a \times 1/2$, or they may be added to $a/2 - 1$, $a/2 - 2$, etc. The resultant vector is combined with the orbital momentum L to give J . Thus with a two-electron system we may have the electron spins adding to give a resultant of 1, or they may be opposed to give 0. Combination of these two possibilities with L gives $J = L$, $L + 1$, and $L - 1$ for the first, and $J = L$ for the second. In these combinations we need consider only positive values; i.e., there is no difference between $J = 1/2$ and $J = -1/2$. The result is that for two electrons the J value for an S term may be 1 or 0; for a P term, 0, 1, 2 or 1; etc. Those terms for which the sum of the electron spins (Σs) is 1 are triple if L is one or more, and therefore these are said to form a *triplet system*. Since all the terms correspond-

ing to zero sum of the electron spins are single, we speak of them as belonging to a *singlet system*.

In Table 1, we present the J values for various values of L and the sum of the electron spins (Σs). From an inspection of this table, we see that the maximum number of terms obtained for a particular pair of values of L and Σs is $2\Sigma s + 1$. This number, which we shall designate as τ , is called the *multiplicity*.⁸

TABLE 1
VALUES OF J CORRESPONDING TO VARIOUS VALUES OF
 L AND Σs

$L \backslash \Sigma s$	0	1/2	1	3/2	2	5/2
0	0	1/2	1	3/2	2	5/2
1	1	3/2, 1/2	2, 1, 0	5/2, 3/2, 1/2	3, 2, 1	7/2, 5/2, 3/2
2	2	5/2, 3/2	3, 2, 1	7/2, 5/2, 3/2, 1/2	4, 3, 2, 1, 0	9/2, 7/2, 5/2, 3/2, 1/2
3	3	7/2, 5/2	4, 3, 2	9/2, 7/2, 5/2, 3/2	5, 4, 3, 2, 1	11/2, 9/2, 7/2, 5/2, 3/2, 1/2
4	4	9/2, 7/2	5, 4, 3	11/2, 9/2, 7/2, 5/2	6, 5, 4, 3, 2	13/2, 11/2, 9/2, 7/2, 5/2, 3/2
	Singlets	Doublets	Triplets	Quartets	Quintets	Sextets

2.23 Notation. The complete description of a term by means of quantum numbers may be written $n^{\tau}L_J$. In this expression, instead of using the number for L , we shall use the appropriate letter, as previously given. The value to be used for n depends on the point of view. In the early literature, it was customary to assign n the value 1 for the lowest term involved in the arc spectrum. Thus for the alkali atoms the lowest state was designated as the $1S$ (or $1^2S_{1/2}$). More recently, n has been taken as 1 for the innermost shell of electrons and the lowest term involved in the arc spectrum

⁸ In books on atomic spectra, S is written for Σs . This is not to be confused with the spectrum terms, which are also designated by S . In order to avoid such confusion, we shall use Σs only in this book.

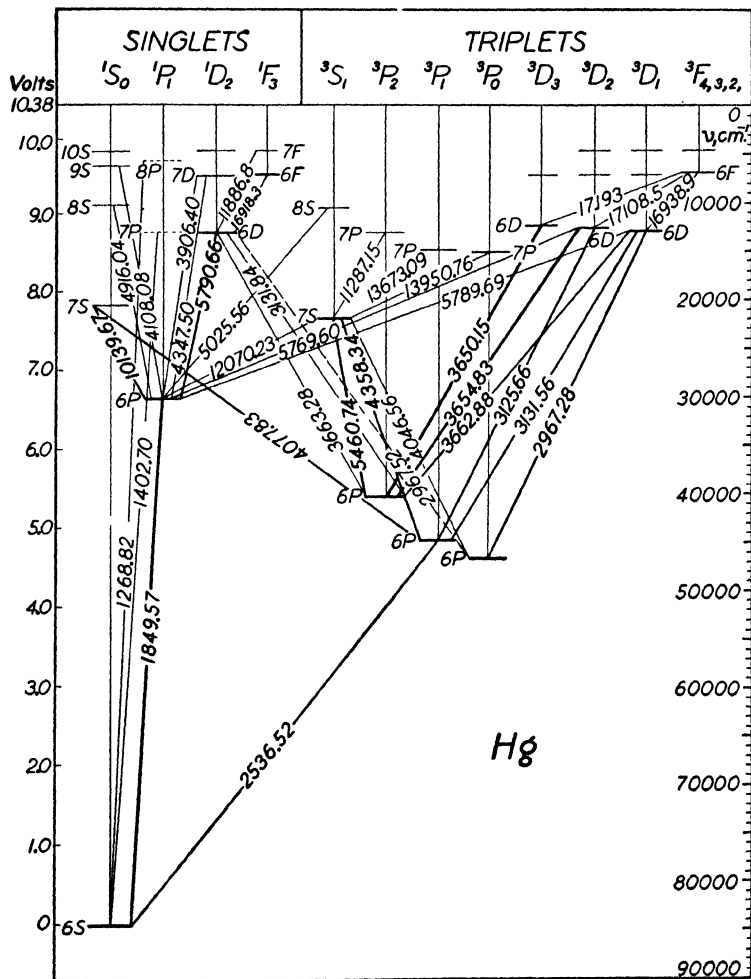
is given a value consistent with this. On such a basis, the lowest term for lithium is $2\ ^2S_{1/2}$; for sodium, $3\ ^2S_{1/2}$, for potassium, $4\ ^2S_{1/2}$; etc. Which form is adopted is really of little importance, as n is needed only for the purpose of designating the successive terms of a series and there is seldom any doubt as to which term is involved. In this book we shall adopt the latter system, and as a convenience for the student in reading the literature we have prepared in Appendix I a "dictionary" correlating the various notations.

2.24 Designation of spectrum lines. The lines of the atomic spectrum, whether in emission or absorption, are expressed as the difference of two terms; thus the yellow doublet in the sodium is given by $3\ ^2S_{1/2} - 3\ ^2P_{3/2}$ and $3\ ^2S_{1/2} - 3\ ^2P_{1/2}$. Not all combinations are permitted. We have already mentioned the selection rule for L ; namely, $\Delta L = \pm 1$. The selection rule for J is that $\Delta J = \pm 1$ or 0, except that $\Delta J \neq 0$ if $J = 0$. Another, but less rigorous, restriction is that transitions between terms of different multiplicities are of low probability. Such transitions, however, do occur; e.g., the important line in the mercury spectrum at $\lambda = 2536.7\ \text{\AA}$ is due to a transition between the $6\ ^3P_1$ and the $6\ ^1S_0$ states. The high intensity of this line is due to the fact that these two states are the lowest two in the mercury atom between which a transition is permitted by the L and J selection rules. These selection rules apply only to transitions involving the absorption or emission of radiation and do not hold for the energy changes which occur in collisions. In such processes the changes which are in accord with the selection rules are more probable than others, but the others do occur rather readily.

Fig. 3 shows the observed transitions for mercury. This diagram may be looked upon as a means of representing a typical spectrum. In the diagram we see that there are no transitions from the $6\ ^3P_2$ and $6\ ^3P_0$ states to the lowest state $^1S_0$; such transitions are "forbidden" by the selection rule for J . These two ^3P states are called *metastable states*, because the atom cannot go from them to the condition of

lowest energy without the aid of a collision or some other perturbing factor.

2.25 Multiplicity and the periodic table. The types of multiplicity found in the spectrum of any given element are determined from its position in the Periodic Table, as may be seen from a consideration of Table 1. When the number of valence electrons is odd; i.e., if the element is a member



of one of the odd-numbered groups of the Periodic Table, then $2s$ is fractional and we have only even multiplicities. Similarly, the elements in the even-numbered groups have only odd multiplicities. If an electron is removed from an atom with the production of a positive ion, the spectrum of this ion is similar to the spectrum of the atom immediately preceding it in the Periodic Table. For example, if an electron is removed from an aluminum atom to give Al^+ , the spectrum of this ion would resemble that of Mg and, if still another electron is removed to give Al^{++} , the spectrum would become similar to that of Na . The multiplicities associated with each group are shown in Table 2.

TABLE 2
MULTIPLICITIES OF THE ATOMS BY GROUPS

GROUP	I	II	III	IV	V	VI	VII
Multiplicities	Doublets	Singlets Triplets	Doublets Quartets	Singlets Triplets Quintets	Doublets Quartets Sextets	Singlets Triplets Quintets Septets	Doublets Quartets Sextets Octets

2.26 Effect of a magnetic field. We have mentioned that in the presence of an external magnetic field a fourth quantum number M is required for the description of atomic energy states. This number M is the component of J in the direction of the field and is subject to the selection rule $\Delta M = \pm 1$ or 0, except that $\Delta M \neq 0$ if $\Delta J = 0$. Since the applied field has a definite direction, we must consider both positive and negative values of M . Furthermore M must change by integral steps; i.e., it may be $1/2$, $3/2$, $5/2$, etc., or 0, 1, 2, 3, etc., depending on whether J is fractional or integral. It follows that the number of values of M associated with a particular value of J is $2J + 1$. For illustrative purposes let us consider the effect of a magnetic field on the yellow sodium doublet. In Fig. 4 are shown the energy states and transitions in the presence and absence of a magnetic field. The $3\ ^2P_{3/2}$ state is split into four com-

ponents, and the $3\ ^2P_{1/2}$ and $3\ ^2S_{1/2}$ states are divided into two each. The permitted transitions are such that the line $3\ ^2S_{1/2} - 3\ ^2P_{1/2}$ becomes four lines in the presence of the magnetic field, and the $3\ ^2S_{1/2} - 3\ ^2P_{3/2}$ breaks up into six lines. It is apparent that the number of lines formed from a given line upon the application of a magnetic field depends on the J values for the energy levels associated with the given transition. The study of this effect, which is known as

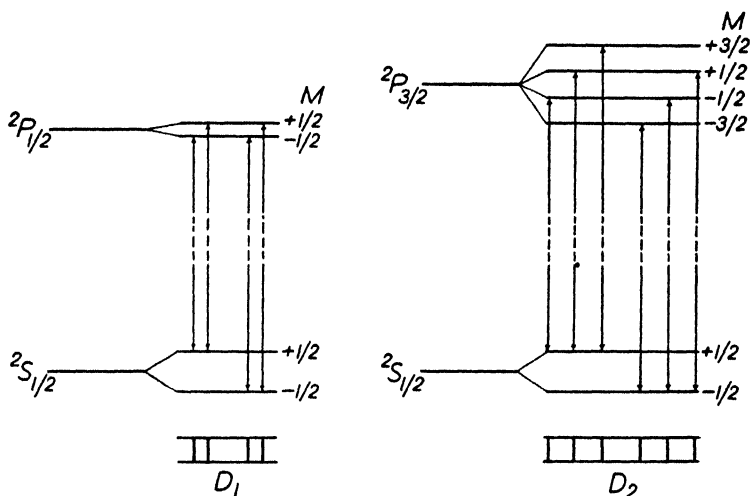


Fig. 4. Magnetic Splitting of Yellow Sodium Doublet; i.e., the D lines $^2P_{1/2} \rightarrow ^2S_{1/2}$ and $^2P_{3/2} \rightarrow ^2S_{1/2}$.

the *Zeeman effect*, is of great value in the classification of spectrum lines. A detailed discussion of such work is beyond the scope of this book.

2.3 Molecular spectra. Just as we find that atoms exist in various discrete states with definite energies, we also find that the energy of a molecule does not vary continuously but is limited to a number of discrete values. With the atoms, we considered that the different possible energy states corresponded to various electronic configurations. In the molecule, we have a much more complicated system in that not only different electronic arrangements are possible but also changes of rotational and vibrational energy must be considered. The Bohr frequency relation $\nu = \Delta E/h$

applies to molecules as well as to atoms, and the ΔE which is involved is the total energy change, i.e., the change due to a change of electronic arrangement plus the change in rotational energy plus the change in vibrational energy. This is often indicated by writing

$$\nu = \frac{\Delta E_e + \Delta E_r + \Delta E_v}{h}$$

in which the subscripts e , r , and v refer, respectively, to electronic, rotational, and vibrational changes.

2.31 Pure rotation spectra. Changes in rotational energy alone are very small in magnitude. Consequently, the frequency of light absorbed or emitted in such a change is low; i.e., these spectra are to be found in the long wave length region of the infrared. According to quantum mechanics the rotational energy of a rigid diatomic molecule is given by

$$E_r = \frac{h^2}{8\pi^2 I} J(J+1) = \frac{h^2}{8\pi^2 I} (J+1/2)^2 - \text{constant} \quad 2-5$$

in which J may assume any positive integral value. I is the moment of inertia of the molecule. In order to simplify the writing of formulas, let $B = h^2/8\pi^2 I$. Application of Bohr's frequency principle gives the frequencies associated with changes of rotation as

$$\nu_r = \frac{\Delta E_r}{h} = B \left[J'(J'+1) - J''(J''+1) \right] \quad 2-6$$

where J' is the rotational quantum number for the upper state and J'' that for the lower.⁹ Only those combinations are observed for which $J' = J'' + 1$. This selection rule reduces the above equation to

$$\nu_r = 2B (J'' + 1); J'' = 0, 1, 2, 3, \text{ etc.} \quad 2-7$$

Spectra of this type have been observed only in absorption. They consist of a series of equally spaced lines, the separation

⁹ The notation J' and J'' for the upper and lower states respectively is adopted in this book because it has become the standard notation among spectroscopists. It is used regardless of which is the initial and which the final state for the process under consideration.

being $2B$. Furthermore these spectra are observed only with molecules which have a dipole moment as, for example, HCl, HBr, and HI. This fact is in accord with the classical picture that associates the absorption or emission of radiation with a change of electric moment. These spectra are found at wave lengths $\geq 40\mu$ and are of no importance photochemically.

2.32 Vibration-rotation spectra. The next simplest spectra involving molecules are those in which we have a simultaneous change of vibrational and rotational energy. The energy of a harmonic oscillator is given by quantum mechanics as

$$E_v = h\omega_e(v + 1/2) \quad 2-8$$

in which ω_e is the fundamental frequency and v is the vibrational quantum number. However, since molecules usually differ appreciably from harmonic character, the energy is better described by a power series:

$$E_v = h\omega_e(v + 1/2) - h\omega_e X_e(v + 1/2)^2 \dots \quad 2-9$$

only the first two terms of which are required in the usual calculation. Here ω_e is the frequency for the lowest state, and X_e is a factor (an experimentally determined constant for the particular electronic level) which allows for the deviation from the harmonic character. The frequencies associated with changes of vibrational energy are obtained by applying the Bohr frequency principle.

$$\begin{aligned} \nu_v &= \frac{\Delta E}{h} \\ &= \left[\omega_e(v' + 1/2) - \omega_e X_e(v' + 1/2)^2 \right] - \\ &\quad \left[\omega_e(v'' + 1/2) - \omega_e X_e(v'' + 1/2)^2 \right] \\ &= \omega_e(v' - v'') - \omega_e X_e(v'^2 - v''^2 + v' - v'') \end{aligned} \quad 2-10$$

In a strictly harmonic oscillator Δv is limited to one, but with actual molecules we always find higher values as well, although the intensities of these bands decrease as Δv in-

creases. In actual spectra we usually have changes in rotational energy as well as vibrational energy; hence the observed frequencies will be given by

$$\begin{aligned}\nu &= \nu_v + B \left[J'(J' + 1) - J''(J'' + 1) \right] \\ &= \nu_v \pm 2B(J'' + 1); J'' = 0, 1, 2, 3, \text{ etc.}\end{aligned}\quad 2-11$$

This equation corresponds to a series of lines proceeding to either side of the frequency ν_v but with no line at ν_v . The separation of the successive lines is $2B$. A more exact treatment shows that a correction term should be introduced into the energy equation with a corresponding change in the frequency relationship which would allow for a deviation from the equal spacing of the rotation lines.

A typical rotation-vibration band, that of HCl between 3μ and 4μ is shown in Fig. 5. The long wave length branch

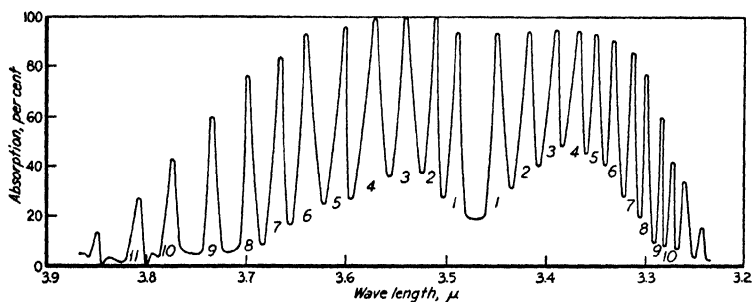


Fig. 5. Rotation-Vibration Spectrum for HCl (at 3.46μ), according to Imes, *Astrophys. J.*, **50**, 251 (1919).

corresponds to $\Delta J = -1$ and is called the negative or *P* branch; the one toward short wave lengths corresponds to $\Delta J = +1$ and is called the positive or *R* branch.

2.33 Electronic bands. By far the most important to the photochemist are the bands which correspond to simultaneous changes of vibration, rotation, and electron configuration. The observed frequencies are given by

$$\nu = \frac{\Delta E_e + \Delta E_v + \Delta E_r}{h} = \nu_e + \nu_v + \nu_r \quad 2-12$$

These bands appear primarily in the visible and ultraviolet portions of the spectrum, and are far more complex in ap-

pearance than the rotation or rotation-vibration bands. A relatively simple system is shown in Fig. 6. The lines appear in groups (or bands) within which the separation of the lines is governed by the changes of rotational energy.



Fig. 6. P_2 Bands.

Let us consider the structure of one of these simple bands for which we may take ν_e and ν_v as constants. The frequencies are given by

$$\nu = \nu_e + \nu_v + B'J'(J' + 1) - B''J''(J'' + 1) \quad 2-13$$

B' and J' refer to the upper state; B'' and J'' , to the lower one. It is to be noted that B' and B'' are, in general, different on account of the change of the moment of inertia with the change of the electronic state. Here, as in the rotation-vibration bands, we have the restriction on J that $\Delta J = \pm 1$, except that, if the molecule is in such a state that it possesses a resultant electronic angular momentum around the axis of rotation, it can change its state of electronic and vibrational excitation without altering its state of rotation; i.e., ΔJ may equal zero. Corresponding to these three possible changes of J , we have three branches to the band. The frequencies of the lines in each branch are given by:

P branch; $J' = J'' - 1$:

$$\nu = \nu_e + \nu_v - (B' + B'')J'' + (B' - B'')J''^2 \quad 2-14$$

Q branch; $J' = J''$:

$$\nu = \nu_e + \nu_v + (B' - B'')J'' + (B' - B'')J''^2 \quad 2-15$$

R branch; $J' = J'' + 1$:

$$\nu = \nu_e + \nu_v + (B' + B'')(J'' + 1) + (B' - B'')(J'' + 1)^2 \quad 2-16$$

The first line in the P branch is at $\nu = \nu_e + \nu_v - 2B''$, and the next ones lie at longer wave lengths (lower frequencies). The Q branch starts at $\nu = \nu_e + \nu_v$, but the next lines lie toward higher frequencies. The R branch starts at $\nu = \nu_e + \nu_v + 2B'$, and progresses toward higher frequencies. The positions of the lines corresponding to high J values in the frequency scale will be determined by the sign of the

quadratic term. If $B' - B''$ is negative, then for high values of J the lines are progressing toward long wave lengths (lower frequencies); whereas, if $B' - B''$ is positive, the opposite is true.

The trends of the frequencies in the three branches are readily seen by reference to a so-called Fortrat diagram,¹⁰ in which the wave lengths (or frequencies) of the lines are plotted as abscissas and the corresponding J values as ordinates. Fig. 7 shows such a diagram, in which $B' - B''$ is

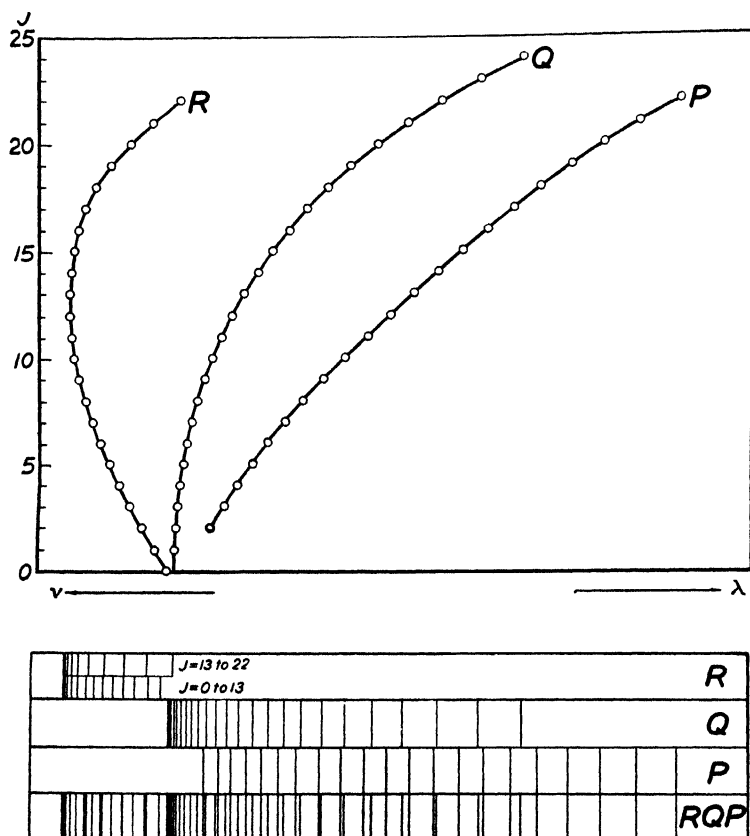


Fig. 7. Fortrat Diagram based on the AlH band at 4241 Å, according to Bengtsson; cf. Sponer, *Molekülspektren*, Julius Springer, Berlin, 1936, p. 54.

¹⁰ Fortrat, Thesis (Paris), p. 109 (1914).

negative. All the curves representing the P , Q , and R branches correspond to quadratic equations and are therefore portions of parabolas. The curvature illustrated in the diagram results in a grouping of the lines at the short wave length end of the Q and R branches, giving rise to what is called a *band head*. It is to be noted that the number of lines present as we approach the band head is not infinite, as in the approach to a series limit in atomic spectra. If $B' - B''$ were positive, the band head would be at the long wave length end of the band.

Since B' is inversely proportional to the moment of inertia in the upper state and B'' to that in the lower state, $B' - B''$ negative means that the moment of inertia increases when the molecule is excited. Such a change would be brought about by increasing the separation of the atoms at equilibrium and therefore decreasing the binding energy. A positive value for $B' - B''$ corresponds to an increase in binding energy and closer approach of the atoms after excitation. Usually we find a decrease in binding energy on excitation, and therefore the band heads appear at the short wave length side of the bands. The cyanogen band at 3883 Å and the CO band at 5610 Å are exceptions.

In the preceding paragraphs we have dealt with the rotational structure of the spectrum of diatomic molecules, which requires the consideration of only one moment of inertia. Certain simple polyatomic molecules, such as CO_2 , CS_2 , COS , N_2O , and C_2H_2 , have been found to have a rotational structure similar to that of diatomic molecules, and therefore are said to be linear molecules. In general the rotation of a polyatomic molecule must be described by considering three moments of inertia corresponding to three axes of rotation. The details of the rotational structure for complex molecules are of little importance to the photochemist at the present time. Just as in the simpler case of the diatomic molecule, the larger the moment of inertia, the smaller is the separation of the lines in the spectrum. For most of the polyatomic molecules we shall consider later in this book, the moments of inertia are so large that the rota-

tion lines have not been resolved in the spectroscopic studies.

2.34 Multiplicity in molecular spectra. Even with diatomic molecules we find that the spectra are more complex than we have indicated. Just as in atomic spectra the simple Bohr picture had to be modified to account for the multiplet structure, in molecular spectra we must introduce additional quantum numbers to allow for the fact that most bands do not have only one P , Q , and R branch but usually show several. Corresponding to the S , P , D , etc. terms in atomic spectra, we have Σ , Π , and Δ terms in molecular spectra.¹¹ They correspond to the values 0, 1, and 2 respectively of a quantum number Λ . This Λ is only partially analogous to the L in atomic spectra, as it specifies, not the total resultant angular momentum of the electrons, but the component of this momentum in the direction of the axis of the molecule. The selection rule is also different in that $\Delta\Lambda = 0$ or ± 1 . That is, we may have transitions between two Σ or two Π terms as well as between a Σ and a Π term, or a Π and a Δ term.

If the molecule consists of two identical atoms, there is a further distinction to be made, namely, between odd and even terms usually designated by the subscripts u and g ¹² respectively. A term is odd or even according to the symmetry properties of the eigenfunction $\psi(x_1, x_2, x_3, \dots)$, which represents the molecular term. Here x_1, x_2, x_3 , etc. are the coordinates of the respective electrons. If each x is replaced by $-x$, the eigenfunction is reflected about the center of gravity of the molecule. It may be shown that under such circumstances the eigenfunction is either unchanged or its sign is changed. In the first case the term is called even, in the second odd. A selection rule says that odd terms combine only with even, and vice versa; i.e., $\Sigma_u \rightarrow \Sigma_g$ is permitted, but not $\Sigma_u \rightarrow \Sigma_u$. These conditions

¹¹ We shall consider only the relatively simple cases of diatomic molecules; cf. cases (a) and (b) of F. Hund, *Z. Physik*, **36**, 657 (1926). For a more complete discussion, the reader is referred to H. Sponer, *Molekülspektren*, Julius Springer, Berlin, 1936.

¹² The subscripts u and g correspond to the German terms *ungerade* and *gerade*.

also apply when the two atoms are nearly alike as, for example, in the chlorine molecule $\text{Cl}^{35}\text{Cl}^{37}$.

To continue the analogy to atomic spectra, we designate the multiplicity of the Σ , Π , etc. terms by a superscript; thus, ${}^3\Sigma$ analogous to ${}^3S$. This multiplicity is equal to $2S + 1$ in which S is the vector sum of the electron spins.¹³ For an odd number of electrons, S is fractional ($1/2$, $3/2$, $5/2$, etc.); for an even number of electrons, it is integral (0 , 1 , 2 , etc.). The multiplicity is therefore even for an odd number of electrons and odd for an even number of electrons. As most normal molecules contain an even number of electrons, it is obvious that in photochemistry the odd multiplicities occur much more frequently than the even ones. Transitions from a state of one multiplicity to a state of different multiplicity occur, but the probability is not great except in the molecules of the heavy elements.

We must consider now the coupling of the electronic spin with the orbital momentum. Only two cases will be considered here. The first, Hund's case (a), is found in a large number of heavy molecules, in which the term splitting due to the electronic spin is large compared to the separation of the individual rotational terms; the second, Hund's case (b), is usually found in Σ terms and in many Π and Δ terms of light molecules, in which the separation due to spin is small compared to the separation of the rotational terms.

In the discussion of the first of these two cases, we must introduce a new quantum number Σ , which is the component of S along the molecular axis. It may assume the values S , $S - 1$. . . $-S$. The selection rule is that $\Delta\Sigma = 0$. The sum $\Lambda + \Sigma$ may be written as a quantum number Ω which, on account of the selection rules for Λ and Σ , obeys the rule $\Delta\Omega = 0$ or ± 1 . Just as in atomic spectra the various terms of a multiplet are distinguished by writing the J value as a subscript, here we may distinguish the different terms of a molecular multiplet by writing the Ω value as a subscript. Thus the ${}^3\Pi$ terms are ${}^3\Pi_0$, ${}^3\Pi_1$, and ${}^3\Pi_2$. The

¹³ Care must be taken to distinguish between the different uses of the letter S . A similar confusion exists in the use of Σ .

selection rules $\Delta\Sigma = 0$ and $\Delta\Omega = 0, \pm 1$ are not strictly valid for heavy molecules.

In the second case, Hund's case (b), the effect of the electronic spins is small compared to the rotational effects. The quantum number Σ is no longer required; instead we have a quantum number K , which is the resultant of a coupling of the orbital momentum of the electrons and the angular momentum of the atomic nuclei. The selection rules for this type of band are $\Delta\Lambda = 0, \pm 1$ and $\Delta K = 0, \pm 1$. The slight coupling of K with S gives rise to J , the total angular momentum. For each value of K , there are $2S + 1$ values of J which determine the multiplicity.

One additional point must be discussed, namely, the designation of rotation terms as positive and negative. A rotation term is called positive if reflection of the coordinates of all of the particles (electrons and atomic nuclei) about the center of gravity of the molecule does not change the sign of the eigenfunction. If the sign changes, then the term is designated as negative. A selection rule states that only transitions between a positive and negative term can occur. In a Σ state, the terms are alternately positive and negative as the rotational quantum number increases. In Π and Δ states, the situation is more complex. For molecules exhibiting what is known as Λ doubling,¹⁴ the terms are split into two components one of which is positive and the other negative. At vanishingly small doubling this energy difference between the positive and negative components becomes zero.

A Σ^+ or Π^+ state is one in which the lowest rotational term is positive, and correspondingly Σ^- and Π^- refer to states in which the lowest term is negative. It may be shown that with this designation the selection rules forbid transfers of the type $\Sigma^+ \rightarrow \Sigma^-$, but permit those such as $\Sigma^- \rightarrow \Sigma^-$.

In the case of molecules consisting of two identical atoms, in addition to classifying the rotational terms as positive or negative and odd or even, we may group them as symmetrical or antisymmetrical in terms of the nuclear coordinates.

¹⁴ Cf. H. Spöner, *Molekülspektren*, Julius Springer, Berlin, 1936, p. 87.

For the symmetrical terms the eigenfunction is unchanged in sign when the nuclei are interchanged, and changes sign for the antisymmetrical terms. In a series of rotation terms the states are alternately symmetrical and antisymmetrical. On the basis of the positive-negative and odd-even classifications the symmetrical terms are positive and even or negative and odd, and the antisymmetrical ones are negative and even or positive and odd. According to the selection rules we have given, there can be no transitions between the symmetrical and antisymmetrical terms.

The last statement leads to the conclusion that the molecules of a substance X_2 can be divided into two groups which may be distinguished from each other and which will not change into each other under ordinary conditions. Such a separation has been accomplished in the case of hydrogen, and the two forms have been named *ortho* and *para hydrogen*. In the lowest electronic state of the hydrogen molecule, the electronic spins are always antiparallel, but the nuclear spins (one-half of $h/2\pi$ for each nucleus) may be either parallel or antiparallel.¹⁵ In para hydrogen we have antiparallel nuclear spins and even-numbered rotational states; the ortho hydrogen has parallel nuclear spins and odd-numbered rotational states. The relative amounts of the two forms present are determined by the statistical weights of the states. Practically, at room temperature this reduces to twice the sum of the nuclear spins plus one; i.e., it is 3 for the ortho and 1 for the para form. Corresponding to these values, ordinary hydrogen is three-fourths ortho. At very low temperatures, the para form is present in the zero rotational state and the ortho in the first rotational state. The latter may therefore be considered metastable. Bonhoeffer succeeded in catalyzing the transformation and prepared practically pure para hydrogen. At ordinary temperatures the transformation of the para hydrogen to the equilibrium mixture is catalyzed by atomic hydrogen and a

¹⁵ Heitler and London, *Z. Physik*, **44**, 455 (1927).

number of other substances. We shall discuss these reactions in greater detail in a later chapter.¹⁶

A discussion of the possible terms which may be formed by bringing together two atoms in specified electronic states is beyond the scope of this book. Such information has been summarized in tabular form by Mulliken.¹⁷ Usually it is of no great importance to the photochemist whether or not he knows the exact designation of a level. The important point is to know what states might exist, in order to be able to decide whether or not such effects as predissociation (cf. Chapter IV) may occur.

The study of the spectra of polyatomic molecules has not progressed to a point which permits the designation of states and statements of selection rules such as we have just given for diatomic molecules. No doubt, various types of electronic and rotational states exist and there are selection rules governing transitions between them. Since the selection rules for diatomic molecules are broken down by external fields (magnetic fields or molecular fields in collisions), it would not be surprising to find the selection rules for polyatomic molecules less rigid than those for diatomic molecules. We shall find it convenient to draw analogies with the diatomic systems when discussing polyatomic molecules, but such comparisons will have only qualitative significance.

2.4 Vibrational structure of electronic bands. For a given electronic configuration in a diatomic molecule, the vibrational energy has been given as

$$E_v = hc\omega_e(v + 1/2) - hc\omega_e X_e(v + 1/2)^2 \quad 2-17^{17a}$$

In this equation, ω_e and X_e are characteristic of the particular electronic state; hence, if we introduce a change in the

¹⁶ For a more detailed discussion of ortho and para hydrogen, cf. A. Farkas, *Orthohydrogen, Parahydrogen, and Heavy Hydrogen*, Cambridge University Press, 1935.

¹⁷ Mulliken, *Rev. Mod. Phys.*, **4**, 26 (1932); Kronig, *Molecular Structure*, Cambridge University Press, 1935.

^{17a} The factor c appears in the energy equations when the frequency ω_e is expressed, as is usually the case, in wave numbers, ν/c , instead of absolute frequency.

electronic arrangement, a new set of vibrational states is set up. Associated with each of these vibrational states will be a set of rotational states, but for simplicity we shall ignore them in the following discussion. The transitions between the various vibrational levels of one electronic state and those of another are illustrated in Fig. 8. There is no selection rule which limits the change in vibrational quantum number in transitions of this type, but in actual cases the observed bands are determined by the properties of the molecule. (This will be discussed more in detail in a later section.) Differentiation of the energy equation 2-17, above, gives

$$\frac{dE_v}{dv} = hc\omega_e(1 - X_e - 2X_ev) \quad 2-18$$

which shows that the separation of the vibrational levels associated with any electronic state decreases as v increases, becoming zero when $v = (1 - X_e)/2X_e$. Strictly speaking this equation applies to the zero lines of the bands (i.e., no rotation), but for practical purposes it is usually applied to the band heads. Thus, if we consider the series of band heads corresponding to transitions from $v' = 1$ to various values of v'' , we find that they converge toward low frequencies (i.e., long wave lengths); whereas, if we consider the transitions in which v' varies and v'' is constant, the convergence is toward high frequencies. Usually only a small number of the possible combinations of v' and v'' are observed.

In polyatomic molecules the vibrations are much more complex. The number of degrees of freedom with respect to vibration is $3n - 6$ (n is the number of atoms in the molecule)

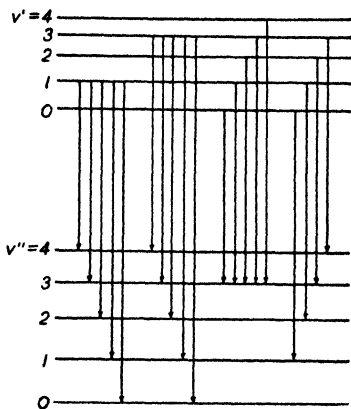


Fig. 8. Transitions between Vibrational Levels of two electron states of a diatomic molecule.

in the general case, or $3n - 5$ if the molecule is linear. The spectra corresponding to such systems are extremely complex and have not been interpreted in detail, except in a very few cases. Fortunately, in our study of photochemistry it is usually necessary to know, not the details of structure of the bands, but merely whether we have to consider the activated molecule or some dissociation products in order to draw conclusions concerning secondary processes. The methods used to obtain such information will be discussed in Chapter IV.

2.5 Potential energy curves. It has been found that the explanations of the behavior of photoactivated molecules can be greatly simplified by the use of diagrams representing the potential energy of the molecule as a function of the separation of the atoms. As a simple example we may consider the diagram (Fig. 9), which is essentially that used by Lochte-Holtgreven¹⁸ in his discussion of the spectrum of S_2 . The lowest energy state of the sulfur atom is a $^3P_2$ level. If we bring together two such normal atoms, the potential energy may vary (depending on the conditions of approach) according to any one of the curves, $^3\Sigma_g^-$, $^1\Sigma_u^-$, or $^3\Pi_u$ in the diagram. Curve $^3\Pi_u$ corresponds to repulsion at all separations of the atoms. In the other two curves we have an attraction which increases as the atoms approach; however, this effect is overcome by the repulsive forces at small distances, causing the curve to rise steeply and form a minimum. Such a minimum always exists when a stable molecule is formed. The fourth curve in the diagram represents the interaction of a sulfur atom in the ^3P state with one in the ^1D . Other electronic energy levels in the molecule could be represented by curves similar to these. The minima in the curves for the states of higher energy indicate

¹⁸ Lochte-Holtgreven, *Z. Physik*, **103**, 395 (1936). The figure we use is different from his in that we favor the value of 4.45 e.v. for the dissociation energy of the normal state. This diagram appears to be the most satisfactory available at present for the S_2 molecule. It cannot be considered completely satisfactory as it would indicate a greater ease of quenching the fluorescence than is actually observed (cf. § 3.36). In this section it is used for illustrative purposes only. Cf. Herzberg and Mundie, *J. Chem. Phys.*, **8**, 263 (1940).

that the molecule is stable with respect to the products obtained by following the curve out to large separations of the atoms, although it may be unstable or metastable with reference to other dissociation products or a lower energy state in the molecule.

The minimum in a curve occurs at the mean equilibrium separation of the atoms when the molecule is in its lowest

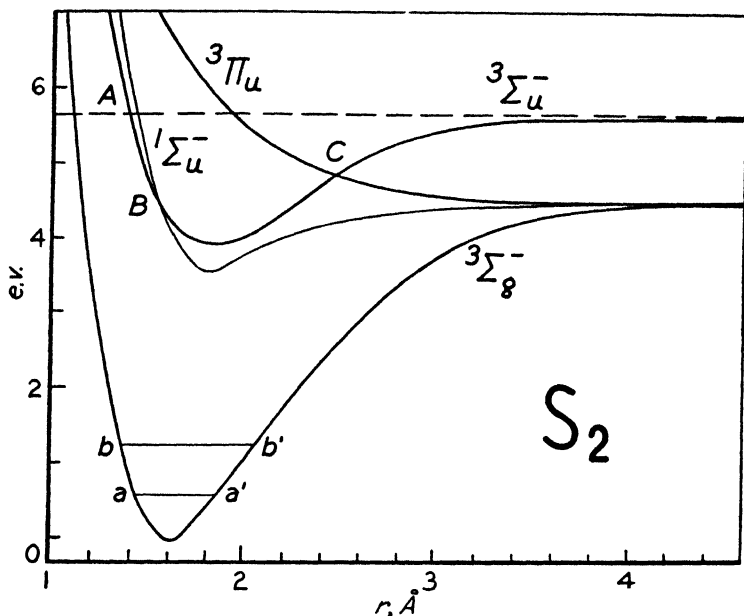


Fig. 9. Potential Energy Diagram for S_2 .

vibrational state. As is apparent from equation 2-17, the atoms are not stationary relative to each other in this lowest state but possess an energy $\frac{1}{2}hc\omega_e - \frac{1}{4}hc\omega_e X_e$ above the minimum of the curve. If we represent this energy by the horizontal line aa' , then the potential energy of the molecule during a vibration would be represented by the motion of a point along the curve from a to a' . The kinetic energy at any point would be represented by the vertical distance between the line aa' and the curve. Higher vibrational energies would be represented by motion along the curve between points such as b and b' . The depth of the minimum

is a measure of the heat of dissociation. Here we must distinguish between the heat of dissociation measured by calorimetric or other measurements, which corresponds to the height from the line aa' to the horizontal line representing dissociation, and the maximum vibrational energy, which is measured from the bottom of the minimum.

2.51 Morse curves for the potential energy of molecules.

No exact mathematical expression has been obtained for these potential energy curves, but several approximate ones have been proposed. The form of the function for stable molecules is apparent from a consideration of our diagram. If we write P.E. = $f(r)$, $f(r)$ must approach a constant value asymptotically at large values of r and must rise rapidly to high positive values when r is small. In between, there must be a minimum. The most widely used function which conforms to these requirements is the one proposed by Morse:¹⁹

$$\text{P.E.} = hc \left(D e^{-2a(r-r_0)} - 2D e^{-a(r-r_0)} \right)$$

In this equation, r_0 is the equilibrium separation of the atoms; D is the maximum oscillation energy and is equal to $\omega_e/4X_e$; and $a = \sqrt{8\pi^2 c \mu \omega_e X_e} / h = 0.2454 \sqrt{M \omega_e X_e}$. M is obtained from the atomic weights by the equation $M = M_1 \cdot M_2 / (M_1 + M_2)$, and μ is the corresponding value for one molecule. This form gives P.E. = $-Dhc$ at $r = r_0$, and P.E. approaches zero for large values of r . The equation is only an approximation, but it seems to fit rather well for non-polar molecules.

If we are dealing with molecules consisting of more than two atoms, the representation of the potential energy as a function of the atomic separations becomes extremely complex. Even for the case of triatomic molecules, unless we assume a linear model or impose some other restriction on the angle between the lines joining the nucleus of one atom to the nuclei of the other two, we must specify three distances in order to specify the potential. Such a system

¹⁹ Morse, *Phys. Rev.*, **34**, 57 (1929).

requires four dimensions for its graphical representation (one potential energy plus three distance coordinates). The linear model can be represented in three dimensions, or even in two if we make plots analogous to contour maps. In such a case the behavior of the molecule may be represented by the rolling of a ball on the surface which represents the potential energy. With more complex molecules the number of dimensions required for a graphical representation increases rapidly, eliminating the possibility of setting up a clear physical picture. However, we shall see that the ideas obtained from the simple pictures can be carried over to the complex systems, with certain reservations.

2.6 The uncertainty principle. In the preceding section we have assumed that we could describe the motion of the atoms in a molecule accurately. Actually it has been shown by Heisenberg that there must always be a certain inexactness to our description of any state. This statement is known as the uncertainty principle and is expressed quantitatively by $\Delta p_i \cdot \Delta q_i = h/2\pi$, in which Δp_i is the uncertainty in the momentum and Δq_i that of the position. Another form of this statement which we shall find very useful is that $\Delta E_i \cdot \tau = h/2\pi$ in which ΔE_i is the uncertainty in the energy and τ is the life period of a given state. Strictly speaking, therefore, instead of drawing lines in Fig. 9 to represent the variations in the potential energy, we should draw broad smears in such a manner that any potential energy curve drawn represents what might be called the center of gravity of a smear or the locus of the most probable values of the energy for a given separation of the nuclei. The uncertainty principle was actually present in Planck's original work, although it was not recognized as such. In his work the position q and the momentum p were described by a point in the area $\Delta p \cdot \Delta q$, but there was no specification as to how Δp and Δq were to be taken. That indefiniteness is equivalent to the statement given above.

CHAPTER III

PHOTOACTIVATION AND THE PROPERTIES OF PHOTOACTIVATED MOLECULES

I. Physical Effects

3.1 Photoactivation. In the preceding chapter it has been pointed out that atoms and molecules can exist only in certain definite energy states which are characteristic of the particular atom or molecule under consideration. The absorption or emission of radiation is associated with a change from one of these states to another. Photochemistry is concerned primarily with the absorption process, as it is by this means that the molecule is put into a reactive form. The number of light quanta of a given frequency which will be absorbed by a system depends both on the number of molecules in the light path that are in the energy level (or levels) which can absorb that frequency and on the transition probability. The temperatures used in the study of photochemical reactions are such that most of the molecules are in the lowest electronic state and in the first few vibrational levels of that state. Many rotational states are represented. The distribution of molecules among the various possible energy states is given quantitatively by the equation

$$\frac{n_i}{n_0} = \frac{p_i}{p_0} e^{-(E_i - E_0)/RT} \quad 3-1$$

In this equation, n_i and n_0 are the number of molecules in the i th and zero states respectively; p_i and p_0 , the statistical weights of these states; E_i and E_0 , the energies per mole; R is the gas constant per mole; and T , the absolute temperature. From this equation it is apparent that, as $E_i - E_0$

increases, the number of molecules in the i th state decreases rapidly.¹

3.11 Laws of absorption. The idea that the absorption is proportional to the number of absorbing molecules leads directly to the two general laws of absorption: Lambert's law, and Beer's law. Lambert's law states that the absorption is proportional to the thickness of the absorbing layer, other factors being constant. Beer's law states that the absorption is proportional to the concentration of the absorbing substance. Mathematically expressed, Lambert's law is $-dI/dx = kI$, and Beer's law is $-dI/dc = k'I$; in integral form, they become $I/I_0 = e^{-kx}$ and $I/I_0 = e^{-k'c}$. We shall usually use the combined form:

$$\frac{I}{I_0} = e^{-\epsilon cd} \quad 3-2$$

in which c is the concentration in moles per liter; d is the thickness of the absorbing layer; and ϵ is a constant, the absorption coefficient, which is determined by the nature of the absorbing substance and the wave length of the light under consideration. There are certain limitations in the use of these laws which must be clearly recognized. For the above equation to hold, ϵ must be a constant. There are many factors which may cause variations in ϵ . The laws are theoretically exact only for a single frequency and a single molecular species. The absorption coefficient ϵ depends on the frequency and on the nature of the absorbing molecule. Often the statement appears in the literature that the absorption of light by a given substance does not obey Beer's or Lambert's law. Such deviations are caused by the experimental conditions and do not represent any fundamental inaccuracy in those laws.

In the first place, actual measurements are always carried out with a range of frequencies for which ϵ may not be the

¹ For a detailed discussion of the calculation of statistical weights, the student is referred to any standard work on statistical mechanics. In considering the distribution of molecules among vibrational states, it is sufficient to assume $p_i/p_0 = 1$. If we are dealing with electronic states in atoms or with rotational states in molecules, $p_i = 2j + 1$.

same. Fortunately, in continuous absorption (such as very frequently occurs in photochemical reactions), the change of ϵ with frequency is so gradual that equation 3-2 will hold if any ordinary monochromatic light source is used and the number and character of the absorbing molecules remain constant. Very marked deviations are found in systems in which line absorption (either of atomic lines or the individual rotational lines in band spectra) occurs. In such cases ϵ is not constant across even one line, but varies from a very high value at the center of the line to very low values at the edges. As light passes through such an absorbing medium, the frequencies corresponding to the centers of the absorbing lines will be removed first, and then those frequencies toward the edges of the lines. The apparent value of ϵ will change from a high value to a low one. Such behavior is exhibited in the absorption of the *D* lines of sodium by sodium vapor. In that case there are also deviations caused by introducing inert gases, which increase the width of the absorption line. These systems deviate in an experimental sense from both Beer's and Lambert's laws.

Deviations from Beer's law may also be caused by a change in the number or nature of the absorbing molecules as the concentrations are changed. Thus, in a mixture of NO_2 and N_2O_4 , an increase of pressure results in the formation of more N_2O_4 at the expense of NO_2 . The absorption coefficients of the two molecular species are not the same; therefore, as the pressure is increased, the apparent value of ϵ will approach that of N_2O_4 . Lambert's law may hold for a mixture of this kind since the composition is not a function of the thickness of the absorbing layer. Even if there is not sufficient interaction of the molecules in a given system to result in the formation of new molecules, it is still possible to have deviations from Beer's law at high concentrations, because the transition probabilities are affected by the environment. The magnitude of such effects cannot be predicted; therefore, in any case where there may be any doubt as to the validity of Beer's and Lambert's laws, an experimental test should be made.

3.2 Reactions of the photoactivated molecule. After an atom or molecule has absorbed a quantum of light, it is in an unstable state and will enter into one of the following processes:

(1) Return to the normal state with the emission of one or more quanta of light. This is called *fluorescence*.

(2) Dissociate into smaller particles.

(3) Return to the normal state as a result of a collision in which the previously absorbed energy is converted into kinetic energy or vibrational energy of the colliding molecules. The term *collision of the second kind* is usually applied to this process. Originally that name was given to collisions in which excitation energy was converted into translational energy, but it is now generally applied to all collisions in which excitation energy is transferred from one atom or molecule to another, or converted into the translational and vibrational energy of both.

(4) Enter into a chemical reaction with another molecule.

3.21 Mean life of an activated molecule. The relative probabilities of the four types of processes depend on many factors such as the amount of energy absorbed by the molecule originally, the concentration of molecules in the vicinity of the excited molecule, and the nature of those molecules. The time that the molecule remains in the activated state is usually spoken of as the *life period* of the activated state for any given set of conditions. Often in photochemistry we desire to know the life period if the experimental conditions are such that processes (3) and (4) above may be neglected. This might be called the "natural" life period of the state. If the absorbed energy is not sufficient to cause any dissociation, we may limit ourselves to (1), but otherwise such a possibility must be considered. Both (1) and (2) are unimolecular processes; hence, if we designate the activated molecule as M^* , we may write

$$-\frac{d(M^*)}{dt} = k_1(M^*) + k_2(M^*) = (k_1 + k_2)(M^*) \quad 3-3$$

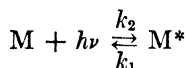
in which k_1 and k_2 are the specific reaction rates of processes (1) and (2) respectively, and (M^*) is used to designate the

concentration of the activated molecules. Integrating this rate expression, we have

$$-\ln(M^*) = (k_1 + k_2)t + \text{integration constant} \quad 3-4$$

Now the average life τ is the time necessary for M^* to drop to $1/e$ of its initial concentration² (in the absence of any process which forms M^*); it follows that $\tau = 1/(k_1 + k_2)$. If no dissociation process is possible or if the probability that such a process will occur is small compared to the probability of radiation, then $\tau = 1/k_1$.

3.22 Correlation of absorption coefficient and transition probability. The constant k_1 is also called the *transition probability* for the change from the higher to the lower state with the emission of light. It is possible to correlate this constant, and hence the average life τ , with the absorption coefficient. Consider a system in equilibrium with radiation as represented by the equation



The constants k_2 and k_1 represent the specific reaction rates of the direct and reverse reactions respectively. The rates of the reactions are:

$$\frac{d(M^*)}{dt} = k_2(M)\rho_\nu \quad 3-5a$$

$$-\frac{d(M^*)}{dt} = k_1(M^*) \quad 3-5b$$

in which ρ_ν represents the concentration of energy of frequency ν . At equilibrium these two rates are equal.³

$$k_2(M)\rho_\nu = k_1(M^*) \quad 3-6$$

$$\frac{(M^*)}{(M)\rho_\nu} = \frac{k_2}{k_1} = \text{a constant at equilibrium} \quad 3-7$$

² Frequently the reader will find references to the *half-life*, which is defined as the time necessary for M^* to decrease to one-half the initial concentration. Although such a definition is often convenient from an experimental standpoint, the definition we have given for τ is more convenient in theoretical discussions. The *half-life* is equal to the product of τ and the natural logarithm of 2.

³ It is to be noted that an equilibrium of this sort is never actually attained in photochemical experiments.

The constant k_2 is the absorption probability. It is readily shown that k_2 is proportional to the experimentally determined absorption coefficient.^{3a}

It follows that, if the absorption coefficient is high, the transition probability for the reverse process is also high and hence the life of the excited state is short. In order to calculate the life of the excited state of a molecule which absorbs more than one frequency, it is necessary to sum equation 3-7 over the entire range of frequencies corresponding to the transition involved. The summation is required because the life period is determined, not by the transition probability for one frequency, but by the sum of the probabilities of all transitions for which the given state is the upper level; i.e., $\tau = 1/\Sigma k_1$. In cases of continuous absorption, such as are frequently found in solutions or gases at atmospheric pressure, the summation can be carried out graphically. If the absorption spectrum consists of fine lines, the treatment is a little more difficult but can be carried out.⁴

3.23 Life periods of activated molecules. The life periods calculated by these methods show a tremendous range. Thus Childs and Mecke⁴ calculated the life of the $^1\Sigma$ state of oxygen as 7 sec., whereas that of iodine is 10^{-7} sec. Direct measurements of the life periods of excited atoms or molecules are limited to those cases in which the life is short enough to enable the experimenter to work under conditions such that collisional deactivation may be neglected. Wien's method⁵ was to excite the molecules of a gas in a discharge tube in which the cathode plate was pierced by a number of holes so that the positive ions formed could pass through these openings. The ions picked up electrons in the space behind the cathode and emitted light characteristic of the molecule. The intensity of this light at a given distance from the cathode is represented by equation 3-5b; therefore, by studying the variation

^{3a} Cf. R. H. Fowler, *Statistical Mechanics*, Cambridge University Press, 1936, p. 722.

⁴ Cf. Childs and Mecke, *Z. Physik*, **68**, 344 (1931).

⁵ Wien, *Ann. Physik*, **60**, 597 (1919); **66**, 229 (1921); **73**, 483 (1924).

in intensity with the distance from the cathode and determining the velocity of the particles in the beam, it is possible to determine k_1 . The velocity of the particles was determined from observations of the Doppler shift of the line when the beam was viewed end on.

Another experimental arrangement was devised by Webb⁶ and modified by Randall.⁷ In principle, the plan was to excite the molecules electrically and to measure the intensity of the radiation at various times after the excitation process was stopped. For the mechanical details, the reader is referred to the original papers. The life periods measured by this method or by Wien's method range from about 5×10^{-9} sec. to 1×10^{-6} sec. Longer life periods cannot be measured in this way, because the molecular concentrations (i.e., pressures) required for measurable intensities are such that the atoms or molecules would be deactivated by collisions rather than by radiation processes. The method is capable of measuring life periods appreciably less than 5×10^{-9} sec. From the failure to find such short lived states, we may conclude that the probability that an atom or molecule will emit radiation is never high enough to make the average life of the excited state less than that value.

Measurements of the average lives of some metastable states in argon, neon, and mercury have been made by determining the amount of absorption of a line in the spectrum for which the given state is the lower energy level.⁸ The results indicate that the observed lives are fixed by the time necessary for the activated atom to be deactivated either at the wall of the container or by collisions. The numerical values obtained were usually of the order of 10^{-3} sec.

3.3 Fluorescence. The emission as radiation of all or part of the energy absorbed by atoms or molecules is spoken of as *fluorescence*. Theoretically, if an atom or molecule is raised to a higher energy level by the absorption of radia-

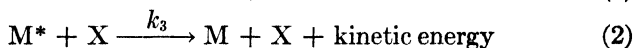
⁶ Webb, *Phys. Rev.*, **24**, 113 (1924).

⁷ Randall, *ibid.*, **36**, 1161 (1930).

⁸ Dorgelo, *Physica*, **5**, 429 (1925); Meissner and Graffunder, *Ann. Physik*, **84**, 1009 (1927); Pool, *Phys. Rev.*, **38**, 955 (1931).

tion, the reverse process is always possible. Practically, if the transition probability is low or if the concentration of other molecules is high, no fluorescence will be observed, on account of the removal of the absorbed energy by collisions. If the absorbed and the emitted light are of the same frequency, the special term *resonance* is often used. Strictly speaking, the term should be used only in this sense; however, it has been used rather extensively in the literature in the discussion of molecular fluorescence excited by monochromatic light at low total pressures, e.g., the resonance series of iodine (see § 3.35).

3.31 Quenching of fluorescence. The photochemist is especially interested in the competition of fluorescence with the other possible reactions of the activated molecule (cf. § 3.2). Many experimental studies have been concerned with the relative rates of deactivation by collision and by fluorescence. These two processes may be represented by the following equations:⁹



In the second of these equations, either or both of the products may be activated without affecting the conclusions we are about to draw. The total rate of deactivation of M^* is

$$-\frac{d(M^*)}{dt} = k_1(M^*) + k_3(M^*)(X) \quad 3-8$$

and the fraction of the activated molecules which fluoresce is

$$\frac{k_1(M^*)}{k_1(M^*) + k_3(M^*)(X)} = \frac{1}{1 + \frac{k_3}{k_1}(X)} = \frac{1}{1 + k(X)} \quad 3-9$$

Now it has been shown by Dunoyer¹⁰ and by Wood¹¹ that at very low pressures all of the absorbed energy is

⁹ In these equations and in later sections, as the occasion shall arise, the letters written above the $\rightarrow$ (k_1 and k_3 here) will be used to designate the specific reaction rates.

¹⁰ Dunoyer, *J. phys.*, (5) **4**, 17 (1914).

¹¹ Wood, *Physical Optics*, Macmillan Company, New York, 1924, p. 160.

emitted as fluorescence. Hence the total number of molecules activated is proportional to the intensity of the fluorescence I_0 , when $(X) = 0$. The intensity of the fluorescence I at appreciable values of (X) is proportional to $k_1(M^*)$. With these substitutions, equation 3-9 becomes

$$\frac{I}{I_0} = \frac{1}{1 + k(X)} \quad 3-10$$

If more than one gas is present, $k(X)$ is replaced by a series of terms $k(X) + k'(X') + k''(X'') \dots$. This equation is valid only if the amount of light absorbed is not affected by the addition of the gas X . If the light absorption is changed, the equation will still hold when we multiply I by the ratio of the light absorbed in the absence of X to that absorbed under the given experimental conditions.

3.32 Resonance of sodium vapor. As a first example of fluorescence let us consider the effects in sodium vapor. The lowest energy level of the atom is the $3^2S_{1/2}$ state; hence the only resonance lines which can be observed are those of the series $3^2S_{1/2} - n^2P_{1/2, 3/2}$ (the *principal series*). Most of the observations have been made with the first doublet of this series, the yellow D lines at 5890 and 5896 Å, but some have also been made with the second doublet at 3303 Å.¹² If the yellow light of a sodium arc is passed into sodium vapor at 200°C., the amount absorbed is greatly affected by the addition of other gases. This effect is due to the fact that the lines emitted from the arc are broadened by the high temperature, pressure, and electric fields in the arc, whereas the absorption lines of the relatively cool vapor are narrow. The width of the absorption lines is increased by the addition of other gases, causing more of the light from the arc to be absorbed.¹³ This effect may be large enough to offset the quenching action of the added gas and cause an increase, instead of a decrease, in the observed intensity of fluorescence as the pressure of inert gas is increased.

¹² Strutt, *Proc. Roy. Soc. (London)*, **A91**, 511 (1915); **A96**, 272 (1920). Christensen and Rollefson, *Phys. Rev.*, **34**, 1157 (1929). Berry and Rollefson, *ibid.*, **38**, 1599 (1931).

¹³ This broadening is due to a perturbation of the energy levels by the fields of force of the other molecules.

Such a complication has been avoided by using what is known as a resonance lamp as the source of the exciting radiation. The light from a sodium arc is passed into a vessel containing sodium vapor at about 200°C., and the fluorescent light from this vessel is used to excite fluorescence in the second vessel, in which the effect of added gas is to be studied. With this arrangement the lines in the exciting beam and those in absorption have the same width. Increasing the width of the absorption lines has little effect on the amount of light absorbed. Mannkopf¹⁴ applied this method to the study of the quenching of the *D*-line fluorescence. The values he obtained for the pressure necessary to reduce the intensity of fluorescence to one-half its original value and for the corresponding values of *k* in equation 3-10 are tabulated in Table 3.

TABLE 3

QUENCHING OF SODIUM RESONANCE RADIATION BY VARIOUS GASES AT 200°C.

Gas Added.....	H ₂	N ₂	He + Ne
Pressure (mm. Hg).....	2.0	1.6	135
<i>k</i>	0.50	0.625	0.0074

It is obvious that the efficiency of the quenching process depends on the nature of the gas to a marked degree. Hámos¹⁵ performed similar experiments with A as the quenching gas and concluded that there was no observable effect.

Wood and Mohler¹⁶ and Lochte-Holtgreven^{16a} excited fluorescence in sodium vapor by using only one of the *D* lines. At low pressure only the line which was absorbed appeared in emission. However, if the pressure was increased either by adding an inert gas or by raising the temperature, the other line appeared; and at a pressure of

¹⁴ Mannkopf, *Z. Physik*, **36**, 315 (1926).

¹⁵ Hámos, *ibid.*, **74**, 379 (1932).

¹⁶ Wood and Mohler, *Phys. Rev.*, **11**, 70 (1918).

^{16a} Lochte-Holtgreven, *Z. Physik*, **47**, 362 (1928).

8 to 12 mm. of A, or Ne and He, the ratio of the intensities of the two lines became the same as when both lines were used for excitation. This increase of the relative intensity of the second line as the pressure is increased is due to the fact that the excited atoms are transferred from one ^2P state to the other by collisions with the other atoms or molecules. If gases such as N_2 or H_2 , which have a strong quenching effect, are added, the intensity ratio never reaches its limiting value.

3.33 Mercury fluorescence. The excited mercury atom offers more possibilities than are found for the sodium atom. The energy level diagram for mercury (Fig. 3) shows that two possibilities of resonance exist. They are the $6\ ^1S_0 - 7\ ^1P_1$ line at 1850 Å, and the $6\ ^1S_0 - 6\ ^3P_1$ line at 2536.7 Å. On account of the strong absorption of the former by the atmosphere, most of the work on the fluorescence of mercury vapor has been done with the 2536.7 Å line (usually designated as 2537 Å). The atom in the $6\ ^3P_1$ state may return to the $6\ ^1S_0$ state with the emission of the absorbed radiation, or it may be transferred by collisions with other atoms or molecules either to the $6\ ^3P_0$ or to the $6\ ^1S_0$ state. If the transfer is to the $6\ ^3P_0$, the atom is left in a metastable state from which it is eventually transferred to the $6\ ^1S_0$ by collisions. According to Orthmann and Pringsheim,¹⁷ the metastable ($^3P_0$) atoms can endure ten thousand collisions before they are deactivated.

Extensive studies of the quenching of the mercury fluorescence have been carried out by Stuart¹⁸ and by Zemansky.¹⁹ Stuart's data show appreciable deviations from the simple law 3-10. This fact was discussed by Zemansky, who showed that the deviations could be accounted for by assuming that some of the atoms were quenched directly and others were transferred to the $^3P_0$ state and then deactivated at the walls. In his own work Zemansky eliminated such disturbing effects and calculated the effective

¹⁷ Orthmann and Pringsheim, *Z. Physik*, **35**, 626 (1926).

¹⁸ Stuart, *ibid.*, **32**, 262 (1925).

¹⁹ Zemansky, *Phys. Rev.*, **31**, 812 (1928); **36**, 919 (1930).

cross sections of a number of gases. These values are listed in the second column of Table 4.

TABLE 4
EFFECTIVE CROSS SECTIONS AND VIBRATION BANDS FOR
MOLECULES WHICH QUENCH MERCURY FLUORESCENCE

Gas	$\sigma^2 \times 10^{16}$ cm. ²	Band Center μ	E volts	$E - 0.218$
O ₂	13.9	—		
H ₂	6.01	—		
CO	4.07	4.66	0.265	0.047
NH ₃	2.94	6.132	0.202	-0.016
CO ₂	2.48	4.88	0.253	0.035
H ₂ O	1.00	6.267	0.197	-0.021
N ₂	0.192	—	0.288	0.070
CH ₄	0.0596	7.67	0.161	-0.057
C ₂ H ₆	0.415	6.85	0.180	-0.038
C ₄ H ₁₀	4.11	5.67	0.218	0.00

The first two of the gases, hydrogen and oxygen, quench the fluorescence by returning the atom to its lowest state. In the case of hydrogen, there can be no doubt that this process results in the formation of atoms. The production of such atoms by Hg in the $^3P_1$ state has been demonstrated chemically by Cario and Franck.²⁰ Meyer²¹ has shown that they are also formed if the excited Hg atoms are in the $^3P_0$ state. Senftleben²² has demonstrated the formation of the atoms by the increase in the heat conductivity of the gas on illumination.

The mechanism whereby the excitation energy is utilized to bring about the dissociation of the hydrogen molecule is not clearly established. Kaplan²³ suggested that the energy given up by the mercury atom raised the hydrogen molecule to another electronic state in which it is unstable. According to the most recent ideas concerning the energies of these electronic states, such a transfer is impossible, as the next

²⁰ Cario and Franck, *Z. Physik*, **11**, 161 (1922).

²¹ Meyer, *ibid.*, **37**, 639 (1926).

²² Senftleben, *ibid.*, **33**, 871 (1925).

²³ Kaplan, *Nature*, **123**, 162 (1929).

lowest level in the molecule is 8.5 to 9.0 volts²⁴ above the lowest state, whereas the excitation energy of Hg ($^3P_1$) is only 4.86 volts. Such an explanation would be possible for the dissociation of hydrogen molecules by excited Xe atoms, for in that case the energy available is 8.5 volts.²⁵

Other possibilities which have been suggested are: (1) The excitation energy of the mercury atom is converted into vibrational energy of the hydrogen molecule, resulting in dissociation. (2) The activated mercury atom reacts according to the equation $\text{Hg} + \text{H}_2 \rightarrow \text{HgH} + \text{H}$. The hydride is very unstable and decomposes rapidly into mercury and hydrogen. However, its presence has been demonstrated by the appearance of its bands in fluorescence when a mixture of mercury and hydrogen at low pressure is irradiated with the 2537 Å line.

Gaviola and Wood²⁶ presented evidence which could be interpreted as indicating that the hydride is formed in a secondary reaction. On the other hand, Beutler and Rabinowitch,²⁷ from a consideration of a large amount of data, concluded that the Hg ($^3P_1$) dissociates the hydrogen directly, whereas Hg ($^3P_0$) reacts to form the hydride and a hydrogen atom. According to Beutler and Rabinowitch, the surplus energy available in the reaction $\text{Hg}^* + \text{H}_2 \rightarrow \text{HgH} + \text{H}$ is 0.84 volt if the $^3P_1$ state is used, and 0.62 volt if the $^3P_0$ is used. Franck and Sponer²⁸ concluded that the maximum amount of vibrational and rotational energy which the HgH molecule can have is 0.67 volt. It follows that, if the reaction listed above involves the $^3P_0$ mercury atom, the HgH can form with high vibrational and rotational energy; but if the $^3P_1$ atom is used, the HgH formed will have so much energy that it will immediately dissociate into the atoms. Of course, the latter mechanism is not distinguishable in any experimental sense from any other mechanism which brings about a dissociation of the hydrogen. It does, however,

²⁴ H. Sponer, *Molekülspektren*, Julius Springer, Berlin, 1936, p. 372.

²⁵ Calvert, *Z. Physik*, **78**, 479 (1932).

²⁶ Gaviola and Wood, *Phil. Mag.* **6**, 1191 (1928).

²⁷ Beutler and Rabinowitch, *Z. physik. Chem.*, **B8**, 403 (1930).

²⁸ Franck and Sponer, *Nachr. Göttingen Ges.*, 241 (1928).

afford a definite physical picture of how the energy of the activated mercury atom brings about the dissociation.

The other hypothesis which has been mentioned; namely, that the energy of the excited mercury atom is converted into vibrational energy of the hydrogen molecule and thus brings about its dissociation, is difficult to test. In a later section (§ 3.34) we shall consider evidence that the transfer of the electronic energy in an atom into vibrational energy is not an efficient process unless there is such a high degree of resonance that little or none of the energy must be transformed into kinetic energy. This is certainly not true in the case under discussion, as the $^3P_1$ mercury atom has an excess of approximately 0.43 volt which must be converted into kinetic energy. At the present time, therefore, it seems that the most reasonable mechanism for the quenching of the mercury fluorescence by hydrogen is the one involving the formation of a hydride as a transitory intermediate.

The quenching of the fluorescence by oxygen may involve a reaction $\text{Hg}^* + \text{O}_2 \rightarrow \text{HgO} + \text{O}$, analogous to the one suggested for hydrogen; or the energy may be taken up by the oxygen molecule with the production of an activated molecule or atoms. Herzberg²⁹ has studied a series of absorption bands of the oxygen molecule which converge at approximately 2500 Å (5.09 e.v.). These correspond to a *forbidden transition* and hence are very weak in absorption. However, the transfer of the oxygen molecule to the upper electronic state of these bands by collision with a $^3P_1$ mercury atom is quite possible and may have a high efficiency. Since such molecules are metastable and lack only 0.23 volt of the energy required for dissociation, it is to be expected that many of them will be dissociated into atoms. Some mercuric oxide is always formed when oxygen-mercury mixtures are illuminated with the 2537 Å line, but it is impossible to tell whether this is formed as a result of the reaction which has been given or by a reaction of oxygen atoms with mercury atoms. Mitchell³⁰ has suggested

²⁹ Herzberg, *Naturwissenschaften*, **20**, 577 (1932).

³⁰ Mitchell, *J. Franklin Inst.*, **206**, 817 (1928).

that the high efficiency of oxygen as a quencher of the mercury fluorescence is due to the existence of a vibrational level in the molecule 4.86 volts above the normal state. Such an exact resonance might be expected to give a high efficiency for the energy transfer from Hg ($^3P_1$), but would be much less efficient for Hg ($^3P_0$). There is no evidence that such is the case; consequently, the other possibilities which have been mentioned are to be preferred.

All of the other gases listed in Table 4 quench the fluorescence by transferring the mercury atom from the $^3P_1$ to the $^3P_0$ state. This fact is demonstrated by the absorption of the 4047 Å line of mercury, which involves the $^3P_0$ as the lower state ($6\ ^3P_0 - 7\ ^3S_1$), when these gases are added to mercury vapor which is absorbing the 2537 Å line. There is a very marked dependence of the efficiency of this quenching on the magnitude of the energy difference between the two lowest vibrational states of the molecule. These energy differences, tabulated in the fourth column of the table, are obtained from the infrared absorption bands, except in the case of nitrogen. Fig. 10 shows a plot of the effective cross section E against the magnitude of the vibration quantum. It is obvious that the high efficiencies are found in those cases in which the vibrational energy taken up by the molecule is almost exactly the difference $^3P_1 - ^3P_0$. The points are not symmetrically distributed about the value 0.218 volt (the value for $^3P_1 - ^3P_0$), but are displaced slightly toward higher energies. This displacement can be accounted for by assuming that the average kinetic energy at room temperature (0.026 volt) contributes to the total quantity which may be converted into vibrational energy.

These data illustrate a principle first stated by Franck:³¹ the most probable change that will occur in a system involving activated states is the one in which the amount of the excitation energy that is converted into kinetic energy is a minimum. Thus, those molecules which are able to take

³¹ Franck, *Naturwissenschaften*, **14**, 211 (1926).

up the energy ${}^3P_1 - {}^3P_0$ of the mercury atom as vibrational energy are the most efficient quenchers of the fluorescence. It is especially noticeable that the monatomic gases He, Ne, and A, which can take up energies of this magnitude only as kinetic energy, are very poor quenching gases. A striking illustration of this principle is furnished by the

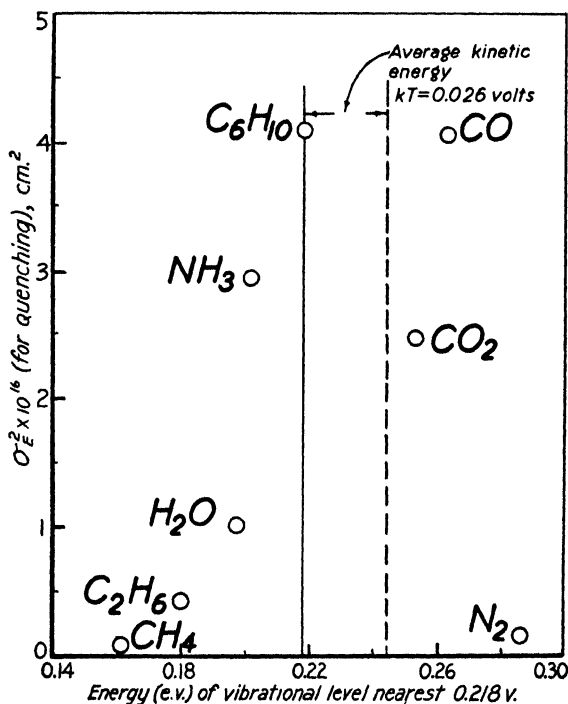


Fig. 10. Effective Quenching Cross Section of Various Substances for Hg Resonance Radiation, according to Zemansky, *Phys. Rev.*, **36**, 919 (1930).

work of Beutler and Josephy³² on the mercury-sensitized fluorescence of sodium. They found a marked preference for the transfer of a sodium atom to the $9^2S_{1/2}$ state on collision with a mercury atom in the ${}^3P_1$ state; the transfer ($3^2S_{1/2} - 9^2S_{1/2}$) requires 4.88 volts.

3.34 Fluorescence of iodine vapor. The fluorescence of

³² Beutler and Josephy, *Z. Physik*, **53**, 747 (1929).

a diatomic molecule, such as I_2 , is much more complex than any found for a monatomic gas. No fluorescence is excited by light absorbed in the continuous portion of the absorption band. In the region of discontinuous absorption, the nature of the fluorescence depends on the absorbed radiation. If the exciting light is so monochromatic that it is absorbed by only one of the fine lines in the iodine bands and if the pressure is very low, then the fluorescence consists

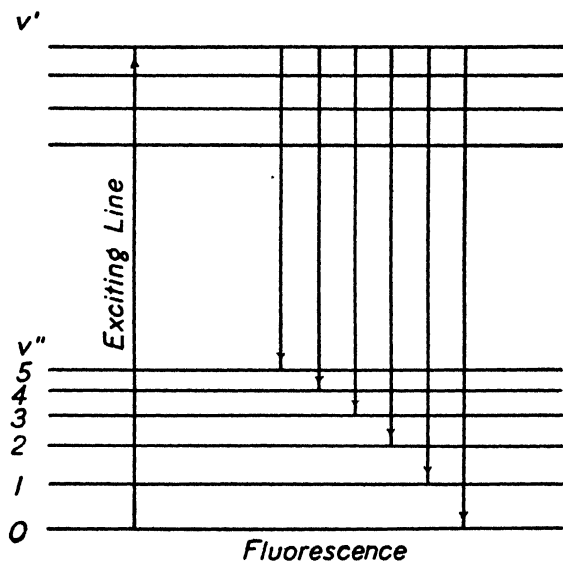


Fig. 11. Fluorescence Excited by Monochromatic Radiation.

of a series of doublets extending from the exciting line toward longer wave lengths. A doublet is formed as a result of the fact that the rotational quantum number J changes by ± 1 as the molecule changes from the upper electronic state to the lower one.

The formation of a series of doublets is readily understood by reference to Fig. 11 which represents the vibrational levels of the upper and lower states. If a molecule in the lowest vibrational state, $v'' = 0$, absorbs light and is shifted to another electronic state with the vibrational quantum number v' , the magnitude of v' will depend on the frequency

absorbed. If the 5461 Å line of the mercury arc is absorbed by iodine, v' is 26. It may then return to any one of the vibrational states, $v'' = 0, 1, 2, 3 \dots$ in the lower electronic level. A doublet is formed for each of these possibilities. Higher values of v'' mean that more of the excitation energy is left in the form of vibrational energy and that less is radiated. It follows that the fluorescence doublets corresponding to the higher values of v'' are of longer wave length than the exciting line. If the light is absorbed by a molecule in one of the higher vibrational levels, the fluorescent light may contain doublets of higher frequency than the exciting light, because of the return of molecules from the upper state to the lowest vibrational states of the normal molecule. In such a case the energy radiated is equal to the sum of the energy absorbed and one or more quanta of vibrational energy.³³

An equation for the frequencies of lines which appear in fluorescence is readily obtained from equations 2-10 and 2-11. It may be written:

$$\nu = \nu_a - \omega_e'' (1 - X_e'')v'' + \omega_e'' X_e'' v''^2 - B''(J' \pm 1)[(J' \pm 1) + 1]$$

3-11

The last term in this equation determines the separation of the lines of each doublet; the positive sign gives one line, the negative the other. The rest of the terms show that the series of doublets converges toward low frequencies (long wave lengths) as v'' increases toward its maximum value, which is determined by the magnitude of X_e .

Two distinct effects are noted when a gas is added to iodine vapor which is fluorescing. One is an expansion of the doublets into bands containing all of the rotation lines; the other is a decrease in the total amount of light radiated (quenching). According to R. W. Wood and Franck,³⁴ the addition of 10 mm. pressure of helium is sufficient to develop

³³ The doublets are often spoken of as Stokes or anti-Stokes, on the basis of a rule, stated by Stokes, that fluorescent light is of the same or lower frequency than the exciting light.

³⁴ R. W. Wood and Franck, *Phil. Mag.*, **21**, 265 (1911).

the whole band, and even 2 mm. causes a considerable portion of the band to appear. At higher pressures, they found a decrease in the total intensity of the radiation and a change in color from green to red.

A striking fact concerning the quenching of the iodine fluorescence is that the rare gases which are very inefficient at quenching the sodium fluorescence reduce the intensity in iodine vapor to one-half the original value when only a few millimeters pressure of these gases has been added.³⁵ Such a great discrepancy is not to be expected if the excitation energy is converted into kinetic energy in both cases. Rabinowitch and W. C. Wood³⁶ offered the explanation that the high efficiency in the case of iodine was due to the additional possibility of quenching by dissociation of the iodine molecule. The energy absorbed in exciting the fluorescence is considerably greater than the heat of dissociation of iodine. It is possible, therefore, for a rare gas atom to quench the excited molecule (without taking up kinetic energy itself) by causing the iodine molecule to change from the state produced by the action of light to one in which it dissociates within the time of one vibration. This process, known as *induced predissociation*, will be discussed more fully in a later section (§4.31). Rabinowitch and Wood concluded from their experiments that the quenching proceeds almost entirely by this path, with only a negligible number of the activated molecules being returned directly to the normal state.

Eliashevich³⁷ studied the efficiency of transfer from one vibrational state to another in the excited state. When the fluorescence was excited by the 5461 Å line of mercury, he observed transfers from $v' = 26$ to $v' = 24, 25, 27$, and 28. If nitrogen was the gas added, the collision radius (calculated on the assumption that a change $\Delta v' = 1$ occurs at every collision) was twelve times the kinetic theory value. With

³⁵ There is no appreciable effect in sodium vapor.

³⁶ Rabinowitch and W. C. Wood, *J. Chem. Phys.*, **4**, 358 (1936).

³⁷ Eliashevich, *Phys. Rev.*, **39**, 532 (1932); *Physik. Z. Sowjetunion*, **1**, 510 (1932); *J. Exptl. Theoret. Phys. (U.S.S.R.)*, **2**, 59 (1932).

hydrogen, the calculated radius was four times the kinetic theory value. The calculations are rather inexact because the radius of the excited iodine molecule is not known accurately.

Ramsauer³⁸ studied the quenching effect of oxygen on the fluorescent series excited in iodine vapor by the 5461 and 5769 Å lines of the mercury arc and by the 5086 Å cadmium line. No appreciable difference was found between the different series, but within a given series the lines at short wave lengths were quenched more than those at longer wave lengths. This fact is in accord with the general change in color of the fluorescence observed by R. W. Wood and Franck³⁴ when quenching gases were added. Koehler³⁹ carried out a similar investigation with argon as the added gas, and found that in this case the series excited by the yellow mercury line was quenched more than the one excited by the green line. This is not inconsistent with Ramsauer's results, since the mechanism of quenching may be different for the two gases. The observed difference in the two series when argon is added is probably due to a greater ease of dissociation from the vibrational state produced by the 5769 Å line than from the state produced by the 5461 Å line. The observed difference is not great but appears to be beyond the limits of experimental error.

3.35 Quenching and energy transfers in other fluorescence spectra. Several attempts have been made to demonstrate the transfer of a molecule from one vibrational or rotational level to another by the addition of a foreign gas. Oldenberg⁴⁰ excited a resonance series in iodine by means of the 1850 Å line of mercury. This series was almost completely quenched by 58 mm. of the noble gases without being expanded into full bands. Similar results were obtained for tellurium by Rosen,⁴¹ and for selenium by Rompe.⁴² On the other hand, sulfur showed a considerable

³⁸ Ramsauer, *Z. Physik*, **40**, 675 (1927).

³⁹ Koehler, *Phys. Rev.*, **44**, 761 (1933).

⁴⁰ Oldenberg, *Z. Physik*, **25**, 136 (1924).

⁴¹ Rosen, *ibid.*, **43**, 69 (1927).

⁴² Rompe, *ibid.*, **65**, 404 (1930).

readiness to transfer to other vibrational and rotational states.

Heil ⁴³ studied and interpreted the effect of helium on the fluorescence of the molecules S_2 , Se_2 , Te_2 . According to his results, the tellurium fluorescence is quenched at practically every collision with helium atoms, and therefore only a small number of transfers from the vibrational state formed in the original excitation to neighboring states can be expected. Actually some transfers corresponding to $\Delta v = \pm 1$ were observed on the addition of nitrogen, argon, or helium. Of these, helium caused the most transfers and was the least efficient quencher. Even at relatively high pressures (100 to 600 mm.), there is no appreciable number of transfers corresponding to $\Delta v > 1$. Selenium shows only a very small amount of transfer and strong quenching. Sulfur, on the other hand, shows very little evidence of quenching and is readily transferred to other states, thus causing the whole band to appear in fluorescence. In the latter respect, sulfur is similar to iodine but the pressure required to develop the bands to the same extent is about ten times as high for sulfur as for iodine.

Lack of information concerning the energy states of the S_2 , Se_2 , and Te_2 molecules makes an exact explanation of these facts impossible. However, Heil has presented a reasonable interpretation. He assumes that, in the S_2 molecule, collisional deactivation returns the molecule to its lowest state. Since this change requires the removal of a large amount of energy as translational energy, the probability of its occurrence is low and thus there is a good opportunity for the occurrence of transfers to other vibrational and rotational states of the excited molecule. In the Se_2 and Te_2 molecules, there is another excited state lying slightly below the one which is produced by the absorption of light. Transfers to this state by collisions occur much more readily than transfers to the lowest state; hence the fluorescence is quenched more readily in these molecules

⁴³ Heil, *ibid.*, **74**, 18 (1932).

than in the S_2 molecule. The separation of the two excited states is assumed to be less for Se_2 than for Te_2 , and therefore the quenching is greater for Se_2 . Correspondingly, the transfers to other rotational and vibrational states occur more readily in Te_2 . The fact that iodine shows so much more transference than quenching as compared to these substances is probably due to the fact that the quenching process in iodine involves a forbidden transition, whereas the changes in S_2 , Se_2 , and Te_2 are assumed to be permitted.

3.36 Conclusions from the study of fluorescence in gases.

A number of important conclusions may be drawn from the results which have been obtained in experiments on the effect of foreign gases on fluorescence. They are:

(1) The change of state which the excited molecule suffers is the one which involves the conversion of a minimum amount of the excitation energy into kinetic energy. The greater the amount of energy which must be converted into kinetic energy in the deactivation process, the smaller the probability that the deactivation will occur.

(2) Changes of vibrational energy corresponding to a change of ± 1 in the vibrational quantum number occur readily; larger changes can be brought about by several collisions.

(3) Rotational energy is altered by collisions more readily than is vibrational energy.

(4) When quenching occurs that is due to a transfer of the activated molecule from one electronic state to another, the efficiency of quenching depends not only on the nature of the quenching molecule but also on the type of transition which occurs in the activated molecule.

(5) Great differences exist in the abilities of different molecules to remove energy from an activated molecule. The most efficient deactivators are those molecules which have two states differing in energy by the same or nearly the same amount as two states in the activated molecule. The data in Table 3 show a forty-fold range in efficiency due to this effect.

3.4 Fluorescence in the liquid state. Most of the substances which fluoresce either in solution or in pure liquid form are complex organic substances; the only inorganic substances are uranium compounds and some of the rare earths. The preceding sections have shown that activated molecules are deactivated very readily by collisions. In solutions, an activated molecule is essentially in a state of collision with the solvent molecules at all times; therefore it is to be expected that the molecules which absorb light will lose the absorbed energy by collisions rather than as fluorescence. The fact that fluorescence is observed indicates that in those cases the alteration in the molecule produced by the light absorption must be very well shielded from the action of the solvent molecules or that a specific mechanism is required for the energy transfer.

The ratio of the number of quanta emitted to the number absorbed has been found to be approximately 1 for dilute solutions of fluorescein, but usually the value is much smaller and varies with the concentration.⁴⁴ Usually the ratio decreases as the concentration of the fluorescent substance increases. For example, the sodium salt of fluorescein does not fluoresce in saturated solutions, and the fluorescence of liquid benzene is less than that of dilute solutions in alcohol.⁴⁵ A possible explanation of this effect is that the absorbing substance is also particularly effective as a deactivating agent.

The life periods of the excited states of some molecules in solution have been determined by Gaviola⁴⁶ to be of the order of 5×10^{-9} sec., or less. The substances studied were some dyes and uranyl sulfate. A considerably longer life, of the order of 10^{-4} sec., was reported for uranyl compounds by Wawilow and Lewschin⁴⁷ and by Perrin.⁴⁸ They used a phosphoroscope which was capable of detecting radiation emitted 10^{-5} sec. after excitation. This delayed emission must be due to the transfer of some of the activated uranyl

⁴⁴ Wawilow, *Z. Physik*, **42**, 311 (1927).

⁴⁵ Riemann, *Ann. Physik*, **80**, 43 (1926).

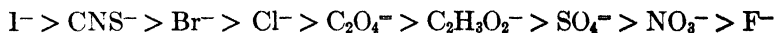
⁴⁶ Gaviola, *Z. Physik*, **42**, 853 (1927).

⁴⁷ Wawilow and Lewschin, *Z. Physik*, **48**, 397 (1928).

⁴⁸ Perrin, *Compt. rend.*, **182**, 929 (1926); **186**, 428 (1928).

ions (or molecules) to a metastable state from which they may return to the normal state either directly or by reactivation to an unstable state. The fact that Wawilow and Lewschin found that the apparent life was decreased by an increase in temperature is evidence in favor of the latter mechanism. Application of equation 3-7 to the data on the absorption of uranyl solutions indicates that the life of the activated state produced by the action of the light must be of the order of magnitude found by Gaviola.

Many observations have been made on the decrease in intensity of the fluorescence of uranyl or dye solutions when other solutes are added. Negative ions have been found to be the most effective for quenching, but recent work of Weber⁴⁹ shows considerable dependence on the nature of the positive ion. He studied the quenching action of various sulfates on the fluorescence of dyes, hoping to find some correlation with the charge of the ion. No correlation was found, although marked differences were discovered. The quenching action of the negative ions⁵⁰ follows the order



when their salts are added to solutions of quinine sulfate, sodium fluoresceinate, or uranyl salts. Specific effects causing deviations from this order will probably be found when more data are available.

The mechanism of the quenching action of the ions is not clear. Franck and Levi⁵¹ have discussed the problem as analogous to the quenching by collisions of the second kind in gaseous systems. Some action of this type may take place; however, a consideration of the data which have been obtained indicates that in many cases the situation must be far more complex. Thus, such a simple picture does not

⁴⁹ Weber, *Z. physik. Chem.*, **B30**, 69 (1935).

⁵⁰ A rather complete list of references on this subject has been given by Weber, *Z. physik. Chem.*, **B15**, 18 (1931); **B30**, 69 (1935). These data are taken from West, Jette, and Müller, *Proc. Roy. Soc. (London)*, **A121**, 294, 299, 313 (1928).

⁵¹ Franck and Levi, *Z. physik. Chem.*, **B27**, 409 (1935).

account for the great difference in efficiency of positive and negative ions; neither does it account for the variations in efficiency with acidity, which have been found in a number of cases.

Furthermore, some of the ions that have been added are known to form complexes with uranyl ion so that the composition of the solution used in a particular quenching experiment cannot be given as x molal UO_2^{++} and y molal X^- , but an allowance must be made for the amount of complex formed. In the case of UO_2^{++} and $\text{C}_2\text{O}_4^{=}$, a very firm complex is formed, as is shown by the change in absorption of the solution as oxalate is added. Whether the ions which are effective quenchers of fluorescence form addition compounds with the dyes is, at present, unknown, although such a possibility must be considered. If complexes are formed, the mechanism of quenching cannot be merely collisions of the second kind; there can be no collisions of that type in the absence of molecules of the assumed kind. Thus the quenching of the uranyl fluorescence by oxalate cannot be due to collisions of the second kind between UO_2^{++} and $\text{C}_2\text{O}_4^{=}$ ions if there are no free UO_2^{++} ions present in the solution. Even if the complex acts the same as the free uranyl ion or dye molecule, the amount of quenching agent assumed to be present must be corrected for the amount which has been used to form the complex. These points have not been considered in the work on fluorescence in solution, and therefore only qualitative significance can be attached to those data. It is to be hoped that, in the future, efforts will be made to express the composition of solutions used in experiments of this kind in terms of the concentrations of the molecules and ions actually present.

CHAPTER IV

PHOTOACTIVATION AND THE PROPERTIES OF PHOTOACTIVATED MOLECULES (CONTINUED)

II. Chemical Effects

4.1 Reactions of photoactivated molecules with other molecules. In the preceding chapter (§3.2) were listed four possibilities for the behavior of a photoactivated molecule. Two of these possibilities, the spontaneous emission of energy and the loss of energy by collisions, were discussed there. In this chapter consideration will be given to the other two possibilities; i.e., the reaction with another molecule, and the dissociation into atoms or radicals.

Reactions of photoactivated molecules with other molecules to form new substances are very rare. One reason for this is, no doubt, that, if a molecule absorbs light readily, the life of the activated state is so short that any reaction which is to occur must take place within a very few collisions and hence must require little or no energy of activation (cf. § 5.21). Even if the molecule does have a long life, the probability of reaction will not be great, unless the heat of activation is very low, because the absorbed energy is likely to be lost by collisions of the second kind.

Most of the reactions of this type which have been studied involve the mercury atom in the 6^3P_1 or 6^3P_0 states. Thus, in the preceding chapter (§3.33), mention has been made of the reaction $\text{Hg}(6^3P_0) + \text{H}_2 \rightarrow \text{HgH} + \text{H}$ and of the possibility of $\text{Hg}(6^3P_{0,1}) + \text{O}_2 \rightarrow \text{HgO} + \text{O}$. The decomposition of nitrosyl chloride¹ has been assumed to involve an activated molecule, but in this case an alternative mechanism which does not include such a possibility is capable of explaining the experimental results (cf. §7.46).

¹ Kistiakowsky, *J. Am. Chem. Soc.*, **52**, 102 (1930).

Reactions of photoactivated molecules with other molecules have been assumed in many other reactions; however, in most cases it has been possible to show that the first step which follows photoactivation is a unimolecular decomposition. The evidence upon which such a decision rests will be presented in the detailed discussion of reaction mechanisms in the later chapters.

4.2 Photodissociation of molecules. The idea that a molecule can be dissociated by the absorption of a quantum of light appeared in the literature at an early date and was used by Einstein ² and by Warburg ³ in their considerations. It was also the starting point in Nernst's mechanism ⁴ for the formation of hydrogen chloride on illumination of mixtures of chlorine and hydrogen. The principal objection raised by opponents of this view was that even such a simple molecule as I₂ can absorb and reemit as fluorescence a quantum having an energy far in excess of the heat of dissociation. Actually this fact shows only that every molecule which absorbs more than its dissociation energy does not necessarily dissociate. It is therefore not possible to state that a molecule is dissociated solely because it has absorbed energy equal to or greater than the heat of dissociation; other evidence must be considered before a decision can be made concerning the result of the light absorption.

The greatest step in setting up a criterion for the direct photodissociation of a molecule was made by Franck in a discussion of the absorption spectra of the halogens.⁵ The absorption spectra of chlorine, bromine, and iodine in the visible and near ultraviolet regions of the spectrum consist of a series of bands which converge to a limit at a wave length slightly less than 5000 Å, followed by a region in which no structure can be detected even with spectrographs of extremely high resolving power. Dymond⁶ showed that, in the case of iodine, fluorescence is excited by light absorbed

² Einstein, *Ann. Physik*, **37**, 832 (1912); **38**, 881 (1912).

³ Warburg, *Z. Elektrochem.*, **26**, 54 (1920).

⁴ Nernst, *ibid.*, **22**, 62 (1916).

⁵ Franck, *Trans. Faraday Soc.*, **21**, 536 (1926).

⁶ Dymond, *Z. Physik*, **34**, 553 (1926).

in the discrete region of the spectrum but not by light absorbed in the continuum. This fact alone suggests that the convergence limit of the bands represents a dividing line between those wave lengths which produce activated molecules and those which produce dissociation, or at least which transform the molecules into some form that is not readily convertible to the original state with the emission of radiation.

Franck's explanation of this fact and the characteristics of the spectra of these elements is best understood by refer-

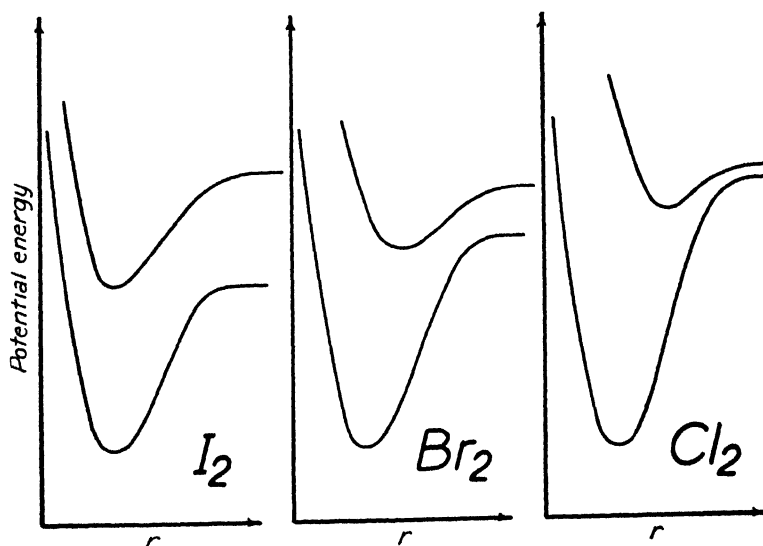


Fig. 12. Potential Energy Curves for the Halogens.

ence to the potential energy diagrams in Fig. 12. The diagrams show only the curves for the upper and lower states. Absorption of a light quantum is represented by a shift from the lower curve to the upper one, and, according to Franck, this change occurs so rapidly that neither the separation nor the kinetic energy of the atomic nuclei changes appreciably during the transfer. In other words, the absorption of a light quantum is represented by a vertical line in the diagram. The shift from one curve to the other represents

the change in potential energy due to the change of the electronic configuration of the molecule. Any kinetic energy that the atoms may have relative to each other at the moment of excitation must also be considered in determining the highest point on the upper curve which will be reached by the absorption of a given quantum of light.

The situation is illustrated by Fig. 13. The energy of the molecule in one of the vibrational levels of the lowest state is represented by the horizontal line AB . In the course of a vibration, the potential energy varies as shown by the

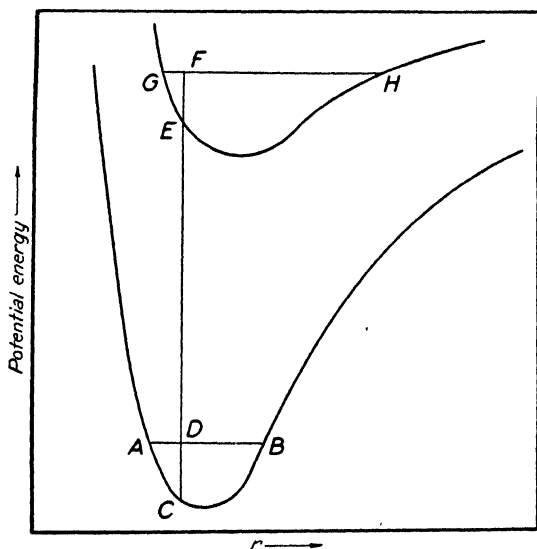


Fig. 13. Energy Relationships in Absorption of a Light Quantum.

curve ACB and the kinetic energy at any stage of the vibration is given by the difference between the line AB and the curve ACB . Suppose that a quantum of light is absorbed at the moment that the nuclear separation corresponds to the point C , the potential energy being given by the point C and the kinetic energy by CD . The light quantum changes the electronic configuration of the molecule with a resultant change of the potential energy from the value at C to that at E . The energy absorbed is represented

by CE . The kinetic energy is unchanged by the transition. Thus the total energy in the upper state at the instant the quantum has been absorbed is represented by prolonging CE by an amount EF equal to CD and drawing the horizontal line GH through the point F . If this total energy in the upper state is less than the dissociation energy of that state, the molecule will vibrate in a manner which may be represented by a point moving back and forth on the upper curve between G and H until it is deactivated by collision, or until it returns to the lower state with the emission of light.

The condition just described is that which prevails in the halogen molecules when the absorption is in the discrete portion of the spectrum. Absorption in the continuum results in the production of a molecule with more energy than is required for dissociation of the upper state, and the molecule dissociates within the time of one vibration ($\sim 10^{-13}$ sec.). The products obtained in this process are, not two normal iodine atoms, but one normal ($^2P_{3/2}$) and one excited ($^2P_{1/2}$). A similar situation exists in the other halogens.

The energy differences ($^2P_{1/2} - ^2P_{3/2}$) for chlorine, bromine, and iodine have been determined by Turner from spectroscopic data.⁷ Subtraction of these values from the energies corresponding to the convergence limits of the bands gives the heats of dissociation of the molecules from their lowest vibrational states into normal atoms. Table 5 (p. 64) shows a comparison of these values with the values obtained from thermal data.⁸ The close agreement between the values calculated from the two completely independent sets of data is in itself a powerful argument in favor of this interpretation of the spectrum. As a matter of fact, in cases of this type where the bands can be followed to the

⁷ Turner, *Phys. Rev.*, **27**, 397 (1926).

⁸ The thermal data do not give the heat of dissociation from any one vibrational level; rather they give the average heat of dissociation of a group of molecules distributed among several vibrational levels. Actually, at ordinary temperatures, most of the molecules are in the first or second vibrational levels, and thus there should be little difference between the thermal and spectroscopic heats of dissociation.

convergence limit, the spectroscopic determination of the dissociation energy is the most accurate one.

TABLE 5
COMPARISON OF THERMAL AND SPECTROSCOPIC VALUES FOR
HEATS OF DISSOCIATION OF THE HALOGENS

Element	BAND CONVERGENCE		$^2P_{1/2} - ^2P_{3/2}$ e.v.	HEAT OF DISSOCIATION	
	Å	e.v.		Spectroscopic e.v.	Thermal e.v.
Chlorine.....	4785	2.575	0.109	2.466	2.3
Bromine.....	5107	2.415	0.454	1.961	1.9
Iodine.....	4989.3	2.472	0.937	1.535	1.5

The formation of atoms by the absorption of light in the continuous portions of the halogen spectra was demonstrated by a number of experiments. Turner⁹ detected absorption of the atomic lines of iodine when iodine vapor was illuminated by light of wave length less than 4990 Å. Bonhoeffer and L. Farkas¹⁰ found a pressure decrease on illuminating iodine vapor, which could be accounted for as a "clean-up effect"; i.e., an effect due to the absorption of iodine atoms on the walls of the containing vessel. Senftleben and Germer¹¹ demonstrated an increase in the heat conductivity of the gases due to the dissociation on illumination.

These experiments suffice to show that atoms are produced as a result of the absorption of light; they do not indicate, however, whether the dissociation process occurs spontaneously after the absorption of a light quantum or whether it is an after-effect due to collisions with other molecules. According to the picture which has been presented, the dissociation must occur within the time of one vibration, which is very much less than the time between collisions. The best evidence for such a direct dissociation is obtained, not from the halogens, but from the alkali halide vapors. The absorption spectra of these compounds

⁹ Turner, *Phys. Rev.*, **31**, 983 (1926).

¹⁰ Bonhoeffer and L. Farkas, *Z. physik. Chem.*, **132**, 255 (1928).

¹¹ Senftleben and Germer, *Ann. Physik*, (5) **2**, 847 (1929).

are continuous with a long wave length limit which moves toward higher frequencies as the heat of dissociation into normal atoms increases. In the case of the iodides and bromides, the continua show several maxima which have been interpreted as corresponding to excitation to various electronic states that lead to dissociation into one normal and one excited atom. Thus, in sodium iodide,¹² the first maximum corresponds to dissociation into two normal atoms; the second, dissociation into a normal sodium and a $^2P_{1/2}$ iodine atom; the third, dissociation into a normal ($^2P_{3/2}$) iodine atom and a $3^2P_{1/2}$ sodium atom; etc.

Terenin's experiments¹³ on the fluorescence of sodium iodide support this interpretation. He found that no fluorescence was excited by absorption in the first two maxima, but that absorption in the next region caused the yellow sodium lines to appear. If a light quantum of sufficient energy to excite the sodium atom to the $4^2P_{1/2}$ state is absorbed, the second doublet ($\lambda = 3303 \text{ \AA}$) of the principal series appears in addition to the yellow lines.

Evidence that these dissociation processes occur without the aid of collisions was presented by Kondratjew.¹⁴ He found that the fluorescence excited in CsI at such low pressures that the mean free path was several millimeters, was confined to the path of the exciting light beam instead of being spread through a large volume, as would be required if a collision were necessary for the dissociation. Furthermore, he found that the intensity of the fluorescence depends only on the light absorbed. If collisions were necessary, the intensity should depend on the light absorbed and the pressure (or, since the light absorbed is proportional to the pressure for small absorption, the intensity would be proportional to the square of the CsI pressure). A final decisive bit of evidence was obtained by Hogness and Franck,¹⁵ who showed that the Doppler broadening of the sodium D

¹² Franck, H. Kuhn, and Rollefson, *Z. Physik*, **43**, 155 (1927).

¹³ Terenin, *ibid.*, **37**, 98 (1926).

¹⁴ Kondratjew, *ibid.*, **39**, 191 (1926).

¹⁵ Hogness and Franck, *ibid.*, **44**, 26 (1927).

lines emitted when light is absorbed by sodium iodide is in agreement with the assumption that the energy absorbed in excess of that required to dissociate the molecule and to excite the sodium atom appears as kinetic energy of the separating iodine and sodium atoms.

The experimental facts which have just been presented demonstrate conclusively that simple diatomic molecules dissociate as a direct result of the absorption of light in the continuous portions of their absorption spectra. Whether the spectrum will consist of a continuum or bands, or a combination of the two is determined by the values of the potential energy in the upper state at nuclear separations such as exist for the lowest or lowest three or four vibrational levels of the normal molecule. If all the potential energies reached by the absorption of light are above the dissociation energy of the upper state, the spectrum will be continuous. If all the potential energies are less than this limit, only bands will be observed. If they lie on both sides of this limit, both bands and a continuum will be observed.

An overlapping of bands and a continuum may arise because the same frequency is absorbed by different vibrational states of the normal molecule, or because transitions occur to two or more different electronic states. This condition is a direct consequence of the Franck-Condon principle; i.e., that the nuclear separations and kinetic energies of the atoms in the molecule do not alter appreciably during the absorption of light. Thus, in the iodine molecule, absorption of light by molecules in the lowest vibrational levels may result either in dissociation or in excitation to a molecule with much vibrational energy. The separation and relative positions of the potential curves representing the electronic states is such that the maximum absorption (i.e., the most probable transition) is close to the convergence limit of the bands.

In the lighter halogens, bromine and chlorine, the binding energy is less in the excited state, and consequently the separation of the atoms is greater when the potential energy

is a minimum. This is shown in the diagram (Fig. 12) by a displacement of the curves for the excited states toward larger values for the nuclear separation. The result is that, when light is absorbed by a normal molecule, the potential energy of the excited molecule most frequently obtained is far in excess of the dissociation energy. This discrepancy is greater for chlorine than for bromine; the maximum in the chlorine absorption is nearly 1500 Å beyond the convergence limit of the bands, but in bromine it is only 900 Å from that limit.

In the alkali halide molecules, the separation of the energy levels involved in the absorption is such that the excited molecule produced by the absorption of light always dissociates. On the other hand, in the case of S_2 the observed absorption always produces a molecule with less energy than is required for dissociation of the upper state.

If a series of bands with a definite convergence limit is observed for a particular electronic transition of a diatomic molecule, it is possible to obtain an accurate value for a heat of dissociation. On the other hand, if only continuous absorption is observed, it is possible to specify only an upper limit for that dissociation energy, since there is no simple relationship between a heat of dissociation and the separation of related energy levels. If a series of bands is observed but a convergence limit is not reached, it is often possible to extrapolate the data to obtain a value for the convergence which would be found if the bands actually extended over such a range. Such extrapolations are subject to many uncertainties, but they may be quite accurate if the frequency range over which the extrapolation extends is small, or at least not large compared to the range over which observations are available.

Various devices have been used to extrapolate the experimental data. Birge and Sponer¹⁶ made use of the fact that, if the energies of the successive vibrational states are

¹⁶ (a) Birge and Sponer, *Phys. Rev.*, **28**, 260 (1926); (b) Birge, *Trans. Faraday Soc.*, **25**, 707 (1929).

given by the equation ¹⁷ $E_v/hc = \omega_0 v - \omega_0 X_0 v^2$, it follows that the dissociation energy from the lowest vibrational state is $D_v = \omega_0/4X_0$. The values of ω_0 and X_0 are obtained from the observed bands. Graphical methods have been proposed by Birge ^{16b} and by Rydberg.¹⁸ Each method has advantages for some particular type of molecule; in general, however, it may be said that the most reliable value for the energy required for dissociation is obtained by using all of the methods and comparing the results.

The heats of dissociation obtained by these methods are not necessarily the same as those observed by thermochemical measurements; in fact, they are usually different. Thermochemical data give the heats of dissociation into normal atoms, whereas the spectroscopic data usually determine the energy required to separate the molecule into one normal and one excited atom. The value corresponding to that obtained from thermochemical data is readily obtained if the amount of excitation energy of the products is known. The values in Table 5 have been calculated in this way.

This kind of dissociation process is not limited to diatomic molecules; it may be found also in polyatomic molecules. Thus, in a molecule such as CH_3I , the absorption of light is accomplished by an alteration in the electronic state in the carbon-iodine bond. Dissociation may then occur into a methyl radical and an iodine atom in a manner entirely analogous to the separation of a diatomic molecule into two atoms. Usually the dissociation of a polyatomic molecule as a result of photoactivation is much more complex and involves mechanisms which will be discussed in greater detail in the later sections of this chapter. However, even in the simplest cases it may not be possible to state from an inspection of the absorption spectrum whether or not dis-

¹⁷ This equation differs from the more exact quantum mechanical equation 2-17, of which it is the predecessor, in that it expresses the energy as a function of v rather than $v + 1/2$. The heats of dissociation obtained by the use of this equation do not differ significantly from those obtained by the use of equation 2-17.

¹⁸ Rydberg, *Z. Physik*, **73**, 376 (1931).

sociation occurs. This difficulty arises from the fact that a spectrum may appear to be continuous because the fine structure is unresolved by any spectrographic equipment. The moments of inertia of most complex molecules are so large that it is impossible to separate the rotational lines in any bands which exist, and the vibrational behavior is often so complex that all that can be observed is an irregular variation in intensity of an apparently continuous absorption. In such cases a decision as to whether or not dissociation occurs must rest on other evidence.

4.3 Predissociation. In the preceding paragraphs we have been concerned only with that type of dissociation in which a bond is broken within the time of one vibration after the absorption of a light quantum. If the absorbed energy is greater than the minimum required to break a bond in the molecule, the possibility of such a dissociation always exists. Such a reaction will actually occur if there exists in the molecule a mechanism which can make the absorbed energy available for such a purpose before it is lost by fluorescence or collisions of the second kind. In gaseous systems the time required for the latter processes is usually of the order of 10^{-8} sec., or greater; i.e., approximately 10^5 times the period of vibration of a simple molecule.

The possibility of delayed dissociation was suggested by Henri¹⁹ in his discussion of diffuse molecular spectra. He was particularly concerned with bands which were neither continuous nor made up of sharp lines but which showed a definite, yet decidedly blurred, structure. Such diffuseness was found in those cases in which the absorption of a light quantum raises the molecule to a higher energy state from which it passes in one or more steps into a dissociated state. Henri called the state produced by the light absorption a "state of predissociation." The fuzziness or complete absence of rotational structure in these bands was said to be due to the fact that the life of the excited state was too short for the rotational energy to be quantized.

¹⁹ Henri, *Compt. rend.*, **177**, 1037 (1923). Henri and Teves, *Nature*, **114**, 894 (1924); *Compt. rend.*, **179**, 1156 (1924).

This idea is expressed more quantitatively in terms of the uncertainty principle. As has been pointed out in an earlier chapter (§ 2.6), the relationship between the uncertainty in the energy of a state and its mean life is given by $\Delta E_i \cdot \tau = h/2\pi$. It follows that, if a state has a very short life, the energy is not sharply defined. Since the spectral frequencies associated with such a state are determined by the differences in energy between that and other states of the molecule, these frequencies will be defined only within certain limits. As a result, the lines observed in absorption will be blurred and, if the lines are close together or the blurring is very great, no line structure will be discernible. It is readily shown by means of the relation given above that, in order for the blurring to be noticeable as an increase over the Doppler broadening of the lines, the life of the excited molecule must be of the order of 10^{-10} sec., or less. As this time is still short compared to the time required for fluorescence or collisional deactivation, it is obvious that this type of delayed dissociation may be of great importance even in some cases where the absorption spectrum shows sharp lines.

The term *predissociation*, which Henri introduced, has been used in many different ways. Some authors have spoken of a spectrum showing predissociation or a predissociation spectrum. Others have definitely applied the term to the last stage of the process, by saying that a molecule predissociates. Since the appearance of the spectrum is not a decisive basis for classification from the standpoint of mechanisms, it is more desirable to define our terms in accordance with the processes which occur. We shall define a simple rupture process as one which occurs at the bond where the light has been absorbed within one vibration period after the act of absorption. All other decomposition processes are classified as predissociation.^{19a} In polyatomic molecules, the meaning of *vibration period* is somewhat vague, since the molecule executes a complex Lissajous figure rather than simple vibrations. However, for the

^{19a} Cf. Burton and Rollefson, *J. Chem. Phys.*, **6**, 416 (1938).

purpose of our definition of predissociation, a vibration period can be considered as the time required if the molecule behaved as if it consisted of two rigid parts vibrating along the bond which joins them.

The picture which is used to indicate the mechanism of the predissociation process is based upon the ideas expressed by Bonhoeffer and Farkas²⁰ and by Kronig.²¹ They suggested that the molecule in the activated state produced by the absorption of a light quantum undergoes a radiationless transfer to another electronic state and separates into two parts in a time of the order of 10^{-13} sec. Such changes have been shown graphically by Herzberg²² by means of potential energy diagrams (Fig. 14, p. 72). The transition from one state to another by this predissociation process must occur without any appreciable change in the separation of the atomic nuclei or in the energy of the system. From the standpoint of the diagram, this means that radiationless transitions occur only at the intersections of two curves.

Actually, according to the uncertainty principle, the properties of a molecule cannot be specified with the precision indicated by the lines representing the variation of potential energy with the nuclear separation. These lines represent mean values for a large number of molecules, or the most probable values of the energy and separation for a single molecule. Therefore the lines must be thought of as blurred and the intersections as regions within which the molecule is in an indeterminate state. If the photo-excited molecule vibrates so that it passes into or through an indeterminate region of this type, there is a possibility that, when it leaves the region, it will be in the other state. The probability that this transfer will occur depends upon the time that the molecule is in this indeterminate condition. This time depends on the kinetic energy of vibration in that region and on the range over which the transition may occur. Whether or not dissociation occurs as a result of the transfer

²⁰ Bonhoeffer and L. Farkas, *Z. physik. Chem.*, **134**, 337 (1928).

²¹ Kronig, *Z. Physik*, **50**, 347 (1928); **62**, 300 (1930).

²² Herzberg, *Z. Physik*, **61**, 604 (1930).

depends upon whether the intersection of curve a , corresponding to the photoactivated molecule, with a' is above or below the dissociation energy of a' . The diagrams in Fig. 14 show several types of intersection which may be conducive to predissociation.

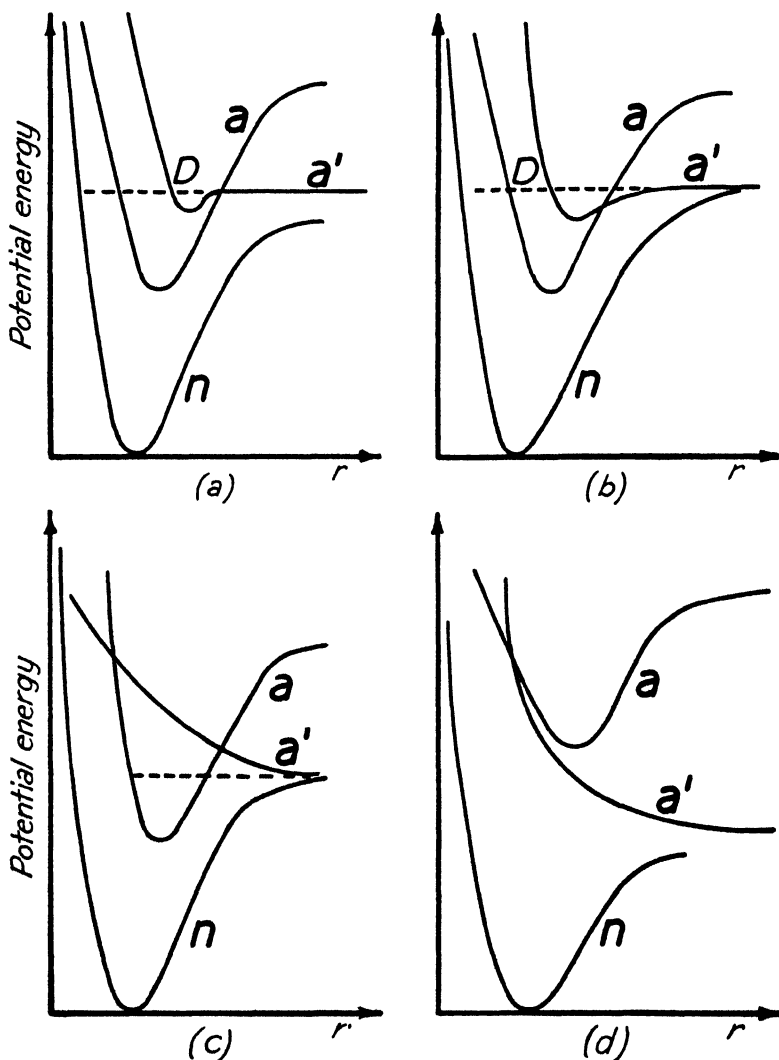


Fig. 14. Relative Positions of Potential Energy Curves in Predissociation.

In diagrams (c) and (d), the intersection of the curves a and a' is above the dissociation energy of a' and therefore dissociation will occur every time a transfer occurs. In diagram (b), the intersection is below the dissociation limit of a' ; hence dissociation will not occur unless the photoexcitation has raised the molecule to a point on the curve a above D . If the system is of the type represented by diagrams (a) and (b), dissociation will appear suddenly at frequencies corresponding to excitation to D or higher. In the other two cases no sharp limit will be found for the frequencies which cause dissociation, since the probability of occurrence of a transition from a to a' increases gradually as the intersection is approached. A crossing of type (c) will come nearer to giving a sharp limit than one of type (d), because in the latter case the close approach of a' to a over a long range causes the probability of transition to rise very gradually. If the probability of transition is great enough to cause a blurring of the fine structure in the absorption bands, it will be observed that types (a) and (b) cause the spectrum to become diffuse abruptly at a wave length corresponding to the dissociation energy of a' . On the other hand, types (c) and (d) cause the fine structure to become gradually less distinct, and it may be difficult to decide on an exact wave length limit for the dissociation.

4.31 Selection rules for predissociation. It is by no means universally true that a transition occurs from one state to another in every case where the potential energy curves for the states cross. Kronig has set up the following selection rules for radiationless transitions between energy states in diatomic molecules:

(1) There shall be no change in the total angular momentum.

(2) Transitions occur only between states of the same multiplicity. (This restriction does not hold for large multiplet separations.)

(3) The quantum number Λ changes by 0 or ± 1 .

(4) Transitions occur from a positive to a positive rotational state, or from a negative to a negative. This is the opposite of the selection rule for radiation transfers.

(5) If the atoms are of the same element, the states involved in a transition are either both symmetrical or both antisymmetrical.

These restrictions apply only in the absence of a perturbing field. In the presence of a magnetic field or collisions with other molecules, the probability of transitions is increased because of the break-down of one or more of the above restrictions. The process in such a case is known as *induced predissociation*.

4.32 Predissociation in polyatomic molecules. In polyatomic molecules the predissociation process is much more complex. Instead of representing the energy levels of the molecule by relatively simple curves such as are shown in Fig. 14, it becomes necessary to think of each level as a complicated hypersurface which represents the potential energy of the system. The molecule in a given electronic state is represented by a point moving on such a surface. In the general case, this point will not execute a simple vibration back and forth about an equilibrium position but will follow a complex Lissajous figure. If the vibrational and rotational energy associated with a given electronic state is sufficient to break one of the bonds in the molecule, there will be one phase of the Lissajous figure which corresponds to the molecule separating into two parts. Such a dissociation may occur within a time comparable to the period of vibration of a diatomic molecule, or it may require several thousand times as long. Thus it is easy to see how a methyl iodide molecule could be excited in such a way that it would dissociate into a methyl radical and an iodine atom. On the other hand, evidence will be presented in a later section to show that the decomposition of formaldehyde into carbon monoxide and hydrogen is a relatively slow process under certain conditions and does not involve a change of electronic state.

According to the definition which has been given for predissociation, we shall consider all cases of delayed dissociation as predissociation processes; this holds whether there is in the potential energy diagram a transition of the point representing the molecule from one hypersurface to

another or whether the dissociation constitutes one phase of the motion on a single hypersurface.

If the point, in the course of tracing a Lissajous figure, comes to the intersection of two hypersurfaces, then there are possibilities of a predissociation process analogous to those which have been discussed for diatomic molecules. It is possible that a set of restrictions analogous to those stated by Kronig for diatomic molecules applies to these transitions from one hypersurface to another, but our knowledge of the properties of the states of polyatomic molecules is not sufficient to express them at the present time. However, the fact that the restrictions for diatomic molecules may be broken down by collisions or by a magnetic field suggests that in polyatomic molecules, which are themselves the centers of complex fields, the selection rules will be much less rigorous. On the other hand, some restrictions must exist, for certain molecules, such as acetaldehyde, can absorb much more than the minimum amount of energy required for dissociation and yet remain in the excited state long enough for fluorescence to compete with the dissociation.

The minimum light frequency which will cause a photodissociation is not necessarily the one which corresponds to the heat of dissociation. The frequencies which will be absorbed by a molecule are determined by the separation of the energy levels for arrangements of the atoms such as exist at the temperature of the experiment. If the molecule vibrates along a single bond in the excited state, a simple rupture into two parts will occur at this bond whenever the energy is equal to or greater than the dissociation energy of that state. Such simple ruptures occur, as a result of the continuous absorption, in the halogens, the alkali halides, and a number of other molecules. Even in these relatively simple cases, the long wave length limit of the continuous absorption does not represent the heat of dissociation of the normal molecule into normal atoms or radicals. In the case of the halogens, the value is higher, corresponding to excitation of one of the atoms in addition to dissociation. In the alkali halides and alkyl halides, the separation of the energy

levels is such that the minimum energy absorbed is greater than that required to split off a halogen atom.

If predissociation occurs, the long wave length limit will correspond to the dissociation only if the intersection of the hypersurfaces (or curves in the simplest case) is at a value of the potential energy equal to or less than this limit. It follows that the long wave length limit of predissociation may be used only as a measure of the upper limit for the dissociation energy.

As the complexity of the molecule increases, the number of hypersurfaces and of intersections of such hypersurfaces increases greatly, and thus there is a greater probability that one or more intersections will occur at such energies that the predissociation threshold will approach the dissociation energy. Hence it is not surprising that such thresholds for complex molecules often coincide approximately with the energy required to break some bond in the molecule.²³ This will probably be found to be especially true in cases of induced predissociation, since in those cases the restrictions have been reduced to a minimum and the probability of transfer from one state to another is a maximum.

The sharpness of the predissociation threshold varies within wide limits. The conditions for diatomic molecules have already been mentioned. In polyatomic molecules the greater complexity of the system introduces the possibility of a much wider spread. Whereas in diatomic molecules the curves corresponding to the energy levels usually cross only once (i.e., once for each predissociation region), the hypersurfaces, which represent the states in polyatomic molecules, may cross at many different values of the potential energy. As the frequency of the absorbed radiation increases (i.e., as the absorbed energy increases), the number of possibilities for transfer to another state increases, and thus the time spent by the molecule in the photoactivated state

²³ It will be seen later (§ 4.8) that, in sufficiently complicated molecules, the minimum energy which must be absorbed to break a bond may be less than the bond strength. (Cf. § 15.48.)

decreases. If this time is short enough to cause a blurring of the spectrum, the blurring will be observed to begin gradually and increase as the absorbed frequency increases, corresponding to the decreasing life of the upper state. Such an effect will be observed only if the lowest point at which the two hypersurfaces intersect is above the dissociation limit of the second hypersurface. If this intersection is below that limit, the predissociation will be found to start abruptly, although the effect may increase somewhat with increasing frequency of the absorbed light.

4.33 Effect of temperature. The effect of temperature on the predissociation limit in polyatomic molecules may be explained on the basis of this same picture.²⁴ At low temperatures the molecule oscillates in its lowest vibrational state in a relatively simple manner. On excitation the separations and kinetic energies of the nuclei are not appreciably altered, and hence the molecule will vibrate in a similar way in the upper state. Under such conditions the molecule may rarely attain a condition corresponding to the intersection of two hypersurfaces; but, if the temperature is increased with a resultant increase in the complexity of vibration in both the upper and lower states, the frequency with which the intersection is reached, and the probability of predissociation, will increase. Such an effect will be most noticeable in those cases where the predissociation threshold is not sharp.

4.34 Tests for predissociation. Several points must be considered in order to determine whether a molecule undergoes predissociation after the absorption of a light quantum. It has already been pointed out that dissociation in a time less than 10^{-10} sec. causes a blurring of the rotational structure in the spectrum. This time is less than the mean time between collisions in gases if the effective molecular diameters are of the magnitude usually assumed in kinetic theory. Therefore, for photochemical reactions in gases, it may be assumed that the primary action of light is to cause dissociation.

²⁴ Henri, *Leipziger Vorträge*, S. Hirzel, Leipzig, 1931, p. 131.

In many systems, especially those involving complex bands, the rotational structure of the bands cannot be resolved; hence their diffuseness, or lack of it, cannot be detected. Sometimes such bands will show a blurring of the band heads which may be used as a criterion for predissociation.

Another test which may be applied is to look for fluorescence in the vapor of the absorbing substance at low pressure. The mean life of the activated state with respect to fluorescence is usually of the order of 10^{-8} sec., or longer; therefore, failure to observe fluorescence is an even more delicate test for predissociation than the blurring of the spectrum. This method is not applicable to systems in which, because of deactivating collisions, the probability of fluorescence is very low. An estimate of the "natural" life (cf. §3.21) of the photoactivated molecule, sufficiently accurate to tell whether collisional deactivation is important or not, may be made by plotting the absorption coefficient against the frequency for various frequencies in the absorption band and comparing the area under this curve with that under the curve obtained from some substance which fluoresces. The greater the area under the curve, the greater the transition probability and hence the greater the chance of observing fluorescence. If these methods fail, specific tests for the dissociation products must be made.

It is more difficult to detect induced predissociation. Some examples are known in which the perturbing effects of other molecules are appreciable at such great distances that the life of the activated state is shortened sufficiently to blur the absorption spectrum. Usually, other evidence for dissociation must be sought in such cases; the methods employed will be discussed in connection with specific examples in the following paragraphs.

4.4 Predissociation in sulfur vapor. The absorption spectrum of the sulfur molecule S_2 has been studied by several investigators.²⁵ A particularly interesting feature is that

²⁵ (a) Henri and Teves, *Nature*, **114**, 894 (1924). (b) Rosen, *Z. Physik*, **43**, 69 (1927); **52**, 16 (1928). (c) Christy and Naude, *Phys. Rev.*, **37**, 490, 903 (1931). (d) Lochte-Holtgreven, *Z. Physik*, **103**, 395 (1936). (e) Cf. Herzberg and Mundie, *J. Chem. Phys.*, **8**, 263 (1940) for a revised interpretation of the S_2 spectrum.

this simple molecule undergoes both spontaneous and induced predissociation. At moderate pressures the spectrum shows a sharp fine line structure from $\lambda = 4100 \text{ \AA}$ to $\lambda = 2799 \text{ \AA}$. At the latter wave length the structure becomes blurred, and at $\lambda = 2615 \text{ \AA}$ the line structure disappears completely. The two diffuse regions are interpreted as two predissociation regions.

Christy and Naude^{25c} ascribed the two changes in appearance of the spectrum to a repulsive state crossing the upper state of the bands at two different points. Lochte-Holtgreven^{25d} showed that such a picture could not be correct, because at very low pressures the lines in the first predissociation region become sharp while those in the second region remain diffuse. This indicates that the process in the first region is an induced predissociation, whereas that in the second region is spontaneous. Thus there must be two different states intersecting the upper state. A transition to the second of these states is permitted by Kronig's selection rules, and the other transition is forbidden by these rules but can occur if the molecule is perturbed by an external field.

The potential energy curves which express these facts are shown in Fig. 9, which is essentially the diagram given by Lochte-Holtgreven. The absorption of a light quantum transfers the molecule from the $^3\Sigma_g^-$ to the $^3\Sigma_u^-$ state. The first predissociation region, which begins with the band for which $v' = 9$, is due to the intersection at *B*; the second, beginning with the $v' = 16$ band, is represented by *C*. The latter transition, from a $^3\Sigma_u^-$ to a $^3\Pi_u$ level, is permitted by the selection rules, but the former is contrary to the rule against changes of multiplicity.²⁶

²⁶ The designation of the second level at *B* as $^1\Sigma_u^-$ is not certain. In a discussion of the corresponding induced predissociation in Te_2 , Kondratjew and Lauris, *Z. Physik*, **92**, 741 (1934), assume that the second level is $^3\Pi_u$, which requires a breakdown of the restriction against transitions from an odd to an even state. For the purposes of this discussion, it is immaterial which selection rule is involved. The extreme ease with which predissociation may be induced can be taken as evidence for the breakdown of the multiplicity rule, as that is one of the least definite.

According to Christy and Naude ^{25c} the first predissociation region begins at $\lambda = 2799 \text{ \AA}$, $v' = 9$, and the blurring reaches a maximum at $\lambda = 2714 \text{ \AA}$, $v' = 11$; after this, the lines become sharper until the second predissociation begins at $\lambda = 2615 \text{ \AA}$, $v' = 16$. At this point, the line structure disappears but begins to reappear in the $v' = 20$ band (cf. Rosen ^{25b}). As v' (and consequently the energy) increases, the molecule passes with increasing speed through the condition represented by the intersection of the two curves. The resulting decrease in the time that the molecule is in that region decreases the chance for an adiabatic transition between the two curves; consequently, the lines become increasingly sharp toward shorter wave lengths. The most favorable condition for a transition is found for a value of v' which requires the molecule to oscillate just to the crossing of the curves. The intersection at B corresponds, therefore, to the maximum diffuseness; i.e., $v' = 11$. Christy and Naude ^{25c} state that the maximum diffuseness in the second region (in the neighborhood of C) is at $v' = 19$. This statement seems a little doubtful in view of the fact that Rosen's observations at low pressure showed some reappearance of structure at $v' = 20$. The explanation of the variation of diffuseness with wave length is exactly the same as for the first region; consequently it may be assumed that the intersection is near $v' = 18$ or 19 .

The beginning of the first predissociation, at $\lambda = 2799 \text{ \AA}$, corresponds quite closely to the dissociation energy of S_2 ; hence the absorption in this region at moderate pressures results in the formation of two normal sulfur atoms. Lochte-Holtgreven has expressed the opinion that dissociation does not occur at these wave lengths but that the molecule is transferred to a metastable state. There are some reasons for assuming that such a transfer may cause blurring of the spectrum in polyatomic molecules (cf. §4.7); however, such an effect does not seem possible in a diatomic molecule. If the initial and final states of the molecule are long-lived, the absorption lines must be sharp. Absorption in the second predissociation region also results in the formation of normal

atoms. No tests for sulfur atoms have been made to test these conclusions.

4.5 Predissociation in iodine vapor. The evidence for dissociation of iodine molecules by light absorbed in the continuous region of the absorption spectrum has already been discussed, and it has been shown that the atoms separate within the time of one vibration. In the banded region of the absorption both the sharpness of the rotational structure and the occurrence of fluorescence show that the molecule exists in the photoactivated state for a time of the order of 10^{-7} sec. Direct evidence that molecules are dissociated as a result of absorption in the banded region of the spectrum was presented by Turner.²⁷ He found that the resonance lines of iodine atoms are absorbed by iodine vapor, which is simultaneously illuminated in the visible band region of I_2 . The effect was greatly increased by the application of a magnetic field or by collisions with other molecules. This is exactly what is to be expected if the dissociation is due to an induced predissociation.

Recently Rabinowitch and W. C. Wood²⁸ have studied this effect more quantitatively. In their experiments the dissociation of the iodine was determined by measuring the light absorbed by the remaining iodine molecules. Their results and their interpretation involve the recombination of the atoms and will be discussed in greater detail in the next chapter. They concluded that argon, nitrogen, and oxygen cause dissociation of the activated molecule at every "gas kinetic" collision. Helium is somewhat less effective, but with a pressure of 500 mm. of that gas all of the activated molecules dissociate.

Evidence of another sort was obtained by Loomis and Fuller²⁹ and by Kondratjew and Polak³⁰ from the study of the absorption spectrum of iodine. They found that the addition of inert gases increased the amount of light absorbed

²⁷ Turner, *Phys. Rev.*, **41**, 627 (1932); *Z. Physik*, **65**, 464 (1930).

²⁸ Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 547 (1936).

²⁹ Loomis and Fuller, *Phys. Rev.*, **39**, 180 (1932).

³⁰ Kondratjew and Polak, *Physik. Z. Sowjetunion*, **4**, 764 (1933).

by those bands for which $\nu' \geq 12$. Three maxima were obtained in the curves of absorption coefficient against ν' at values of $\nu' = 22, 29$, and 39 . This effect was explained as caused by a broadening of the lines in the bands due to the fact that the life of the activated state is shortened by the induced predissociation. The three maxima were attributed to three different regions in which induced transitions can occur.

The energy levels of the iodine molecule are not known with sufficient accuracy to draw an exact potential energy

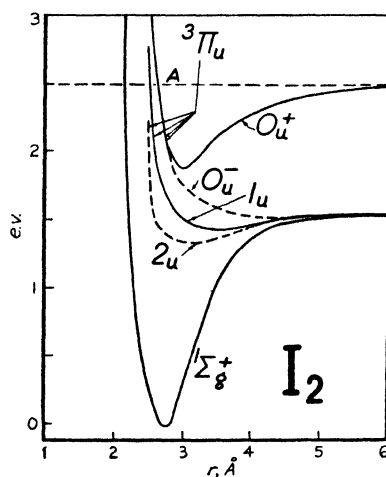


Fig. 15. Potential Energy Diagram for I_2 .

diagram. However, the curves given by Mulliken³¹ suffice for a qualitative discussion of the observed phenomena and are given in Fig. 15. The visible absorption band is associated with the transition $^1\Sigma_g^+ \rightarrow ^3\Pi_{0u}^+$. The dissociation must occur by a transition to one of the other $^3\Pi$ levels, but such transitions are contrary to the selection rules and hence do not occur spontaneously. According to this figure, the most probable transfer is to

the $^3\Pi_{0u}^-$. Such a transition requires that either the selection rule which requires transitions from positive to positive rotational terms in predissociations, or the one which prohibits change of angular momentum in such a process (i.e., that $\Delta J = 0$), must be violated.³² These selection rules are much harder to break down than the one forbidding transitions between states of different multiplicity, such as is

³¹ Mulliken, *Rev. Mod. Phys.*, **4**, 1 (1932).

³² This diagram does not attempt to explain the three crossings indicated by the work of Kondratjew and Polak. The positions of the $^3\Pi$ levels other than $^3\Pi_{0u}^+$ are far from certain. For the purposes of the present discussion, it is immaterial whether or not the designation of the levels is exactly correct.

involved in the induced predissociation of sulfur. Hence the predissociation is not induced nearly so readily in iodine as in sulfur.

4.6 Predissociation in formaldehyde vapor. Formaldehyde is a relatively simple polyatomic molecule which serves to illustrate the predissociation processes in such systems. The absorption spectrum in the near ultraviolet shows a broad band which is characteristic of all the aldehydes and ketones and is generally attributed to the carbonyl group. The statement that the absorption is due to a particular group in the molecule requires some amplification.

According to the Bohr frequency principle, the absorbed frequencies are determined by the changes in energy of the molecule as a whole. It has been found, however, that a comparison of the absorption spectra of a series of compounds (all of which contain a certain characteristic group) shows that all contain a band which may be said to be due to absorption in that group. Thus the near ultraviolet spectra of acetaldehyde, propionaldehyde, *n*-butyraldehyde, and *i*-butyraldehyde differ only in a minor way from one another. It seems reasonable to conclude that the aldehyde group is the effective absorber (§ 8.7) and that this is little affected by the nature of the alkyl radical attached to it. Since formaldehyde and the ketones also have virtually the same band, the locus of the absorption is considered as restricted to the carbonyl group. In terms of the hypersurfaces, which represent the electronic states of the molecule, this statement means that the transition which occurs as a result of absorption in this band is between those hypersurfaces or parts of hypersurfaces where the energy difference is determined primarily by the carbonyl group. The energy absorbed in this way may simply serve as the activation energy for a reaction, such as polymerization, or it may cause a rupture of the molecule. In the aldehydes and ketones, the carbon-oxygen bond in the carbonyl group is never broken but other bonds often are. All such rupture processes are of the type we define as predissociation.

The absorption spectrum of formaldehyde is discrete from 3570 to 2750 Å, and diffuse from 2750 to 2500 Å; a continuous background which begins at 2670 Å extends to shorter wave lengths.³³ Decomposition of the formaldehyde into carbon monoxide and hydrogen occurs as a result of absorption in any of these three regions of the spectrum. The difference in appearance of the spectrum in the three regions corresponds to the existence of three different life periods of the activated state with respect to a decomposition process. The fine-line structure from 3570 to 2750 Å indicates a relatively long life for this degree of excitation. This idea receives further support from the fact that fluorescence has been excited by light of $\lambda = 3530, 3400,$ and 3270 Å .³⁴ No fluorescence has been excited by wave lengths in the diffuse or continuous regions. The abrupt change to a diffuse spectrum at $\lambda = 2750 \text{ Å}$ is due to a new decomposition process which shortens the life of the activated state to a time of the order of 10^{-11} sec., and the continuum at shorter wave lengths indicates a still shorter life.

The close correspondence between the energy of a light quantum $\lambda = 2750 \text{ Å}$ and the energy required to break the carbon-hydrogen bond (approximately 103 kcal.³⁵), and also the fact that hydrogen atoms are produced at shorter wave lengths than 2750 Å but not at longer,³⁶ indicates that, at high frequencies, predissociation results in the formation of H and HCO. At longer wave lengths the energy supplied by the light is not sufficient to break any bond in the molecule; hence the decomposition observed by Norrish and Kirkbride³⁷ must proceed according to some other mecha-

³³ Henri and Schou, *Z. Physik*, **49**, 774 (1929). Herzberg, *Trans. Faraday Soc.*, **27**, 378 (1931). Dieke and Kistiakowsky, *Proc. Nat. Acad. Sci.*, **18**, 346 (1932); *Phys. Rev.*, **45**, 4 (1934). Price, *J. Chem. Phys.*, **3**, 256 (1935).

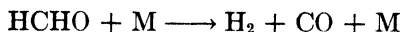
³⁴ Herzberg and Franz, *Z. Physik*, **76**, 720 (1932); Gradstein, *Z. physik. Chem.*, **B22**, 384 (1933).

³⁵ Cf. Trenner, Morikawa, and Taylor, *J. Chem. Phys.*, **5**, 203 (1937); Kistiakowsky, *J. Phys. Chem.*, **41**, 175 (1937).

³⁶ Patat, *Z. physik. Chem.*, **B25**, 208 (1934); Löcker and Patat, *ibid.*, **B27**, 431 (1934). Cf. § 8.72.

³⁷ Norrish and Kirkbride, *J. Chem. Soc.*, 1518 (1932).

nism. Norrish and Kirkbride originally suggested an induced predissociation



in which M may be another formaldehyde molecule. If it is this type of process, addition of inert gases should increase the fraction of the activated molecules which decompose and reduce the fraction which fluoresces. Herzberg and Franz³⁴ report that addition of air up to 100 mm. pressure does not appreciably diminish the fluorescence. This shows that neither nitrogen nor oxygen can dissipate the energy of the excited molecule or induce predissociation. Since both of these gases (especially oxygen, which is paramagnetic) are very efficient at inducing predissociation, it seems reasonable to conclude that in the case of formaldehyde the decomposition at $\lambda > 2750 \text{ \AA}$ is due to a spontaneous process. This is the view at present accepted by Norrish.^{37a}

At these wave lengths the absorption of a light quantum excites the molecule to a state of relatively long life in which it vibrates in a complex Lissajous figure. Eventually the vibration enters a phase that is identical with the separating half of a collision between a molecule of H_2 and one of CO, and the formaldehyde molecule breaks into these products. This reaction may occur either with or without a change of electronic state, i.e., a change from one hypersurface to another. If a change of state were involved, it would be expected that the probability of transfer would be affected by collisions with other molecules. The failure to observe such an effect in the case of formaldehyde suggests that the delayed dissociation in this case is due to slowness in reaching the required phase relationships rather than slowness in transferring to another state.

4.7 Predissociation in sulfur dioxide. SO_2 shows a blurring of the fine structure in the spectrum in two regions. The

^{37a} Cf. Norrish, *Acta Physicochim. U.R.S.S.*, **3**, 173 (1935); *Trans. Faraday Soc.*, **30**, 105 (1934); *Proc. Roy. Soc. (London)*, **A146**, 257 (1934).

first appears gradually at 2800 to 2600 Å; the second begins at approximately 1950 Å.³⁸

Since the minimum energy required for a dissociation process is the 134 kcal. required for the reaction $\text{SO}_2 \rightarrow \text{SO} + \text{O}$, the first region cannot represent a predissociation process in the sense that we have defined the term. The suggestion has been made by Franck, Sponer, and Teller³⁹ that this blurring is due to an induced transfer to a metastable state which causes an abnormal broadening. Such transfers undoubtedly can occur in complex molecules. The diffuseness of the spectrum may be attributed to the fact that the transfer, although it is to a definite quantized state, may occur to so many states that the effect is practically the same as for a dissociation. The much smaller number of possible states in diatomic molecules makes such a process extremely unlikely in such a case, although it was assumed by Lochte-Holtgreven for the first predissociation region of sulfur (cf. § 4.4). In general, it may be said that the more complex a molecule, the greater will be the probability of finding such an apparent predissociation. Most systems which have been studied photochemically do not require the assumption of such a process. For the present at least, it represents an interesting theoretical possibility but not one which is often observed.

The diffuseness which begins at 1950 Å can be attributed to a true predissociation. The corresponding energy, 147 kcal., is 13 kcal. more than is required for dissociation of SO_2 into SO and O . This excess energy probably takes the form of vibrational or kinetic energy of the separating parts.

4.8 General conclusions. The examples which have been cited serve to show that photodissociation is frequently associated with a continuous or diffuse absorption spectrum. However, the photochemical process involved cannot be decided from the appearance of the spectrum alone. Dissociation may occur in a discrete region, and a spectral region which appears to be continuous or diffuse is not

³⁸ For further remarks on the absorption spectrum of SO_2 , see § 7.31.

³⁹ Franck, Sponer, and Teller, *Z. physik. Chem.*, **B18**, 88 (1932).

necessarily an indication of dissociation. Any time that the absorbed energy is greater than that required for the rupture of some bond in the molecule, the possibility of dissociation must be considered, regardless of the character of the absorption spectrum. In diatomic molecules the minimum frequency which will produce dissociation is

TABLE 6
PHOTODISSOCIATION PROCESSES AND THE EFFECTIVE
WAVE LENGTHS

Reaction	Effective λ Å	Reference
$\text{TiCl} \rightarrow \text{Ti}^+ + \text{Cl}^-$	2130	(1)
$\text{TiBr} \rightarrow \text{Ti}^+ + \text{Br}^-$	2010	(1)
$\text{TiI} \rightarrow \text{Ti}^+ + \text{I}^-$	1850	(1)
$\text{PbCl}_2 \rightarrow \text{PbCl}^* + \text{Cl}$		(2)
$\text{PbBr}_2 \rightarrow \text{PbBr}^* + \text{Br}$	1850-2300	(2)
$\text{PbI}_2 \rightarrow \text{PbI} + \text{I}$		(2)
$\text{HCl} \rightarrow \text{H} + \text{Cl}$	2150	(3)
$\text{HBr} \rightarrow \text{H} + \text{Br}$	2500	(3)
$\text{HI} \rightarrow \text{H} + \text{I}$	4000	(4)
$\text{SnCl}_2 \rightarrow \text{SnCl} + \text{Cl}$	1500-1800	(5)
$\text{SnI}_4 \rightarrow \text{SnI}_2 + \text{I}_2$	2500-2150	(6)
$\text{CH}_3\text{HgCl} \rightarrow \text{HgCl} + \text{CH}_3$	2100 (?)	(7)
$\text{HgCl}_2 \rightarrow \text{HgCl} + \text{Cl}$	1850 1900	(8)
$\text{HgBr}_2 \rightarrow \text{HgBr} + \text{Br}$	2100-1900	(8)
$\text{HgI}_2 \rightarrow \text{HgI} + \text{I}$	2200-2100	(8)
$\text{NaI} \rightarrow \text{Na} + \text{I}$	3900	(9)
$\text{KI} \rightarrow \text{K} + \text{I}$	3800	(9)
$\text{CsI} \rightarrow \text{Cs} + \text{I}$	3800	(9)
$\text{NaBr} \rightarrow \text{Na} + \text{Br}$	3100	(9)
$\text{KBr} \rightarrow \text{K} + \text{Br}$	3100	(9)
$\text{KCl} \rightarrow \text{K} + \text{Cl}$	2800	(9)

REFERENCES

- (1) Terenin and Popov, *Physik. Z. Sowjetunion*, **2**, 299 (1932).
- (2) Popov and Neujmin, *ibid.*, **2**, 394 (1932); *J. Phys. Chem. (U.S.S.R.)*, **5**, 863 (1934).
- (3) Coehn and Stuckardt, *Z. physik. Chem.*, **91**, 737 (1916).
- (4) Rollefson and Booher, *J. Am. Chem. Soc.*, **53**, 1728 (1931).
- (5) Neujmin, *Acta Physicochim. U.R.S.S.*, **2**, 595 (1935).
- (6) Terenin, *Nature*, **135**, 543 (1935).
- (7) Terenin, *J. Chem. Phys.*, **2**, 441 (1934).
- (8) Terenin, *Z. Physik*, **44**, 713 (1927).
- (9) Franck, H. Kuhn, and Rollefson, *Z. Physik*, **43**, 155 (1927).

usually somewhat higher than that required for splitting the molecule into normal atoms. The more complex the molecule is, the greater will be the probability that the frequency required for dissociation will correspond to the heat of dissociation calculated from thermal data. It is possible that rupture of the molecule will occur at even lower frequencies by utilization of the energy in the other degrees of freedom, as has been assumed in the discussion of unimolecular reactions.⁴⁰ This effect might cause free radicals to appear in the vapor of certain organic compounds as the result of illumination with light of wave length longer than that corresponding to the energy required to break the carbon-carbon bond in those cases. On the other hand, the cases of SO_2 and I_2 demonstrate that the energy which must be absorbed to cause dissociation may be considerably greater than the minimum required according to thermal data.

4.9 Dissociation processes for which only spectroscopic evidence has been obtained. Many examples of continuous absorption are known which may be interpreted as corresponding to simple dissociation processes. In many of these systems no net reaction is observed because of the rapidity of a reaction which returns the substance to its original state. Table 6 (p. 87) lists a number of typical cases with the effective wave lengths.

⁴⁰ Cf. Kassel, *Kinetics of Homogeneous Gas Reactions*, Reinhold Publishing Corp., New York, 1932, Chapter V; also Franck and Herzfeld, *J. Phys. Chem.*, **41**, 97 (1937).

CHAPTER V

REACTION KINETICS

5.1 Rate determining factors in photochemical reactions.

The rate of any photochemical reaction depends on: (1) the rate of absorption of light; (2) the rates of the secondary steps which follow the photoactivation. The rate of absorption of light is determined by the intensity of the incident light beam and some function of the concentration of the absorbing substance.¹ If there is only one molecular species in the reaction mixture which absorbs the effective light, the form of the concentration function is often determined by the combination of Beer's and Lambert's laws:

$$I_{abs} = I_0 - I = I_0(1 - e^{-\epsilon cd})$$

This may be written as a power series by expanding the exponential:

$$I_{abs} = I_0 (\epsilon cd - \frac{\epsilon^2 c^2 d^2}{2!} + \frac{\epsilon^3 c^3 d^3}{3!} - \dots) \quad 5-1$$

It is obvious that for small absorption ($\epsilon cd \ll 1$) the higher power terms may be neglected and, as a first approximation, the equation may be written

$$I_{abs} = I_0 \epsilon cd \quad 5-2$$

indicating that the rate of light absorption is proportional to the concentration of the absorbing substance.

This equation may be applied in all cases of small absorption in which the concentration c of the absorbing species is known, provided that ϵ is a constant for the range of

¹ The intensity of a light beam is the rate at which it supplies energy per unit area. If we write I equal to the number of photons per unit time, then the intensity at any frequency equals $I \cdot h\nu \div \text{area}$. I_{abs} is therefore a rate of absorption.

wave lengths used in the exciting beam.² Most of the photochemical reactions which have been studied involve a photosensitive substance with a continuous absorption for the effective wave lengths. In such cases the absorption coefficient changes so slowly with wave length that it is essentially constant for any reasonably narrow range of frequencies.

5.11 Efficiency of a photochemical reaction. The quantum theory requires that, when a substance absorbs light, each quantum which is absorbed brings about a change in one molecule. It is possible for one molecule to absorb more than one quantum in successive steps, as has been shown by R. W. Wood's experiments on mercury vapor.³ However, usually the concentration of molecules which have absorbed one quantum is so low that their absorption of further quanta is negligible. There is no positive evidence that such processes are ever of importance in photochemistry. One quantum of light cannot be absorbed by two or more molecules.⁴

These statements are equivalent to saying that the *photochemical equivalence law* (§1.3) holds rigorously insofar as the light absorption process is concerned. The number of molecules which react as a consequence of the absorption of a light quantum may be one, or any number greater or less than one, depending on the properties of the photo-activated molecule. The experimentally determined quantity

$$\gamma = \frac{\text{number of molecules reacting}}{\text{number of quanta absorbed}}$$

is called the *quantum yield*. The observed rate of reaction may be expressed as γI_{abs} , in which γ may be a constant or

² It is to be noted that this approximation is not valid for a system in which mercury vapor is absorbing the light of the mercury arc, because the absorption coefficient ϵ changes even over such a narrow range of frequencies as is found in a single spectrum line.

³ R. W. Wood, *Phil. Mag.*, **50**, 774 (1925).

⁴ We are neglecting such interactions of radiation and molecules as are found in the Compton and Raman effects, since they do not cause an activation of the molecule which has any significance in chemical reactions.

may be some function of the concentrations of the substances present in the reacting system and I_{abs} is expressed as quanta absorbed per unit time.

Since each quantum of light absorbed produces a change in one molecule, one problem of photochemistry is to explain the fact that the observed quantum yields (cf. Table 7) are rarely unity but range from very small fractions to very

TABLE 7
QUANTUM YIELDS OF TYPICAL PHOTOCHEMICAL REACTIONS

Reaction	Effective Wave Length Å	γ	Remarks and Reference
$2\text{NH}_3 \longrightarrow \text{N}_2 + 3\text{H}_2$	2100	0.25	(1) Varies somewhat with pressure and surface area; reaches a maximum at 80–90 mm.
$2\text{O}_3 \longrightarrow 3\text{O}_2$	2080–3130	> 4	(2) Varies with pressure of H_2 , N_2 , O_2 , or other gases present.
$2\text{HI} \longrightarrow \text{H}_2 + \text{I}_2$	2070–2820	2	(3) Constant over a wide range of conditions.
$\text{CO} + \text{Cl}_2 \longrightarrow \text{COCl}_2$	4000–4360	~1000	(4) Varies with the CO and Cl_2 pressures. Also affected by O_2 and impurities.
$\text{H}_2 + \text{Cl}_2 \longrightarrow 2\text{HCl}$	4000–4360	~ 10^6	(5) This is the maximum value observed. Varies with H_2 pressure. Sensitive to impurities.

REFERENCES

- (1) Wiig, *J. Am. Chem. Soc.*, **57**, 1559 (1935); **59**, 827 (1937).
- (2) Heidt, *J. Am. Chem. Soc.*, **57**, 1710 (1935).
- (3) Warburg, *Sitzb. kgl. preuss. Akad. Wiss.*, 300 (1918).
- (4) Bonhoeffer, *Z. Physik*, **13**, 94 (1923); Bodenstein, *Z. physik. Chem.*, **130**, 422 (1927).
- (5) Bodenstein and Winter, *Sitzb. preuss. Akad. Wiss. Physik.-Math. Klasse I*, (1936).

large numbers. Some idea of the range of values encountered is obtained from Table 7, which lists the data for several reactions. The values less than unity may be due to loss of the activation energy by fluorescence or deactivating collisions (cf. Chapter III), or to the reformation of the original substance by recombination of the atoms or radicals produced in the photodissociation. The relative probability of these processes must be discussed for each specific reaction. A quantum yield greater than unity shows that the absorption of light produces an active molecule, radical, or atom which initiates a series of reactions that involve one or more additional molecules of the reactants. Such reactions are generally referred to as *chain reactions* whether the series of reactions is limited to a definite number of steps, as in the decomposition of hydrogen iodide, or includes two steps which are repeated a great number of times, as in the formation of hydrogen chloride from the elements. The number of steps in the chain depends upon the properties of the substances involved in these steps.

5.2 Kinetic theory and rates of reaction. The behavior of the reactive particles produced by the action of light depends, first of all, on the number of collisions between these particles and between these particles and other molecules. According to the kinetic theory, the number of collisions per unit volume of gas is

$$Z = 2n_1n_2\sigma_{12}^2\sqrt{\frac{2\pi RT}{M}} \quad 5-2^5$$

In this equation, n_1 and n_2 are the numbers of molecules of types 1 and 2 respectively, σ_{12} is the mean diameter, M is the reduced mass $M_1 M_2 / (M_1 + M_2)$, and R and T have the customary significance. Equation 5-2 may be condensed to

$$Z = 5.0\sigma_{12}^2 n_1n_2\sqrt{\frac{RT}{M}} \quad 5-3$$

The only uncertain quantity in the equation is the mean

⁵ Kassel, *Kinetics of Homogeneous Gas Reactions*, Reinhold Publishing Corp., New York, 1932, p. 31.

diameter σ_{12} . Many different methods of determining molecular diameters agree on the order of magnitude as 10^{-8} to 10^{-7} cm.; the actual values are spread over that range. As a matter of fact, the diameter of a molecule is not a sharply defined quantity but may be appreciably different for different processes. An extreme example is furnished by Datta's experiments⁶ on the depolarization of the resonance radiation of sodium. It is found that the resonance radiation excited in dilute sodium vapor by polarized D lines is itself polarized. However, at higher pressures the polarization disappears. Even if it is assumed that every collision is effective in causing depolarization, a value is obtained for the collision diameter ten thousand times as great as that calculated from other data. Such extreme variations are not encountered in processes involving chemical reactions; however, a discrepancy of a factor of ten in the collision numbers calculated from the rates of two different bimolecular reactions is within the range permitted by the approximation involved in this calculation.

The mean free path of a molecule of type 1 with respect to collisions with a molecule of type 2 is

$$l_1 = \frac{1}{\sqrt{2} \pi \sigma_{12}^2 n_2} \quad 5-4$$

and the mean free time, i.e., the time between collisions, is

$$t_1 = \frac{1}{5.0 \sigma_{12}^2 n_2 \sqrt{\frac{RT}{M}}} \quad 5-5$$

For gases at atmospheric pressure, the time between collisions is usually slightly greater than 10^{-10} sec.

5.21 Activation energy of a reaction. If every collision results in reaction, the rate of a bimolecular reaction is readily calculated from equation 5-3. For the special case $n_1 = n_2 = 6 \times 10^{23}$ molecules per liter = 1 mole per liter, the result is that approximately 10^{11} moles per liter react per second. Actually such a reaction rate occurs only in

⁶ Datta, *Z. Physik*, **37**, 625 (1926).

a few rare cases; the reactions of atomic hydrogen with the halogens and several other substances are included in such cases. Usually only a small fraction of the collisions cause reaction. The rate of a reaction may be expressed as

$$\frac{dx}{dt} = kf(\text{concentrations})$$

i.e., a constant times some function of the concentrations. The constant k , the specific reaction rate or the rate when all the concentrations involved in $f(\text{concentrations})$ are unity, varies with temperature according to an equation first proposed by Arrhenius:

$$k = se^{-Q/RT} \quad 5-6$$

Q has the dimensions of energy and is called the heat of activation. The factor s includes the number of collisions and any probability factors. The interpretation of this equation is that a reaction occurs only in those collisions in which the energy is equal to or greater than Q . The exponential is the fraction of the number of collisions for which that condition is true. In a strict sense, this interpretation is true only for very simple reactions. The observed specific reaction rate of a complex reaction usually involves the constants of two or more of the steps in the mechanism, and therefore both s and Q are the resultant of the values for those steps (cf. Chapter XI).

Usually the factor s is considered as independent of temperature, although the number of collisions does vary slightly with temperature. If it is desired to consider this variation, 5-6 may be written

$$k = AT^{1/2}e^{-Q/RT} \quad 5-7$$

On taking the logarithm of both sides and differentiating with respect to T , we obtain

$$\frac{d \ln k}{dT} = \frac{1}{2T} + \frac{Q}{RT^2} \quad 5-8$$

The accuracy of the experimental work on gaseous systems does not warrant consideration of a term as small as $1/2T$; it is rarely justified for systems in solution.

5.22 Theoretical basis of activation energy. Numerous papers have appeared in which attempts have been made to calculate the absolute rate of a reaction from a consideration of the properties of the reactants and products and from certain assumptions as to the behavior of the system in the transition state. These methods are directed toward calculation of s and Q in equation 5-6. The values of s obtained from the theoretical considerations seem to be fairly well in accord with the experimental values, but for reactions such as will be discussed in the later chapters of this book the simple collision picture is adequate. It is obvious from an inspection of 5-6 that small errors in the determination of Q will make large errors in s . Thus an error of 1.5 kcal. in Q means an error of a factor of 10 in s .

The attempts to calculate Q on theoretical grounds have not yielded very accurate results. Even those who are making the calculations admit that the error may be as much as 10 kcal., which corresponds to a factor of 10^7 in the rate constant. The inexactness is probably not due so much to the theoretical ideas as it is to the approximations which must be made in making the numerical calculations. The theoretical considerations are of considerable importance because they present an interpretation of activation energy which is quite different from that which appears in the older literature.

London⁷ discussed the energy of two molecules as they approach each other, as a combination of the interactions of the various atoms taken in pairs. As a simple example, consider the variation in the binding energy as an atom X is brought up to a molecule YZ . The interactions to be considered are X - Y , X - Z , and Y - Z . If it is assumed that any one of these interactions is independent of the existence (or non-existence) of the others, the total binding energy of the system may be calculated. It has been found that the most favorable direction for X to approach YZ (i.e., the one involving minimum activation energy) is along the line which is the prolongation of the axis of that molecule.

⁷ London, *Z. Elektrochem.*, **35**, 552 (1929).

Under such conditions the binding energy, according to London, is

$$E = A + B + C + \sqrt{\frac{1}{2}[(a - \beta)^2 + (a - \gamma)^2 + (\beta - \gamma)^2]} \quad 5-9$$

The terms A , B , C , a , β , γ are defined as follows: $A + a$ is the interaction energy of X and Y ; $B + \beta$, that of X and Z ; and $C + \gamma$ that of Y and Z .⁸ These energies, and therefore the total binding energy, vary with the separations of the atoms. In the usual case, as X approaches YZ , the potential energy rises to a maximum and then decreases as the system changes to its final state (for example, $XZ + Y$). If X is brought up to YZ along any other line than the most favorable one, the maximum value of the potential energy will be higher than for the most favorable path. The difference between the maximum value of the potential energy on the most favorable path and the value when X is at a great distance from YZ is interpreted as the activation energy for the reaction of X with YZ . This treatment represents the activation energy as a property of the reacting system rather than as an energy which a particular molecule must have in order to react.

The problem that is encountered in using equation 5-9 in a numerical calculation is to evaluate the interaction energies $A + a$, $B + \beta$, and $C + \gamma$, and to decide on the division of each of these values into the two parts. Eyring and Polanyi⁹ proposed the use of the Morse curves (cf. § 2.51) for the molecules XY , XZ , and YZ for the energies. The division of the energies into the two parts was made with some reference to theoretical calculations on the hydrogen molecule but was essentially arbitrary. Usually a , β , and γ have been considered as approximately 90 per cent of the total binding energy.

⁸ The quantities A , B , C are the coulombic energies, and the quantities a , β , γ are the valence or interchange terms. The significance of this distinction is not important for the purposes of this discussion; it is only necessary to consider that the binding energies may be divided into two parts which enter the equation for the total binding energy as shown in 5-9. For further details, the reader is referred to the original work by London.

⁹ Eyring, *Naturwissenschaften*, **18**, 914 (1930); Eyring and Polanyi, *Z. physik. Chem.*, **B12**, 279 (1931).

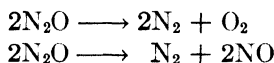
Three serious difficulties enter into this type of calculation. In the first place, it has been found that the maximum corresponding to the activation energy occurs at separations of the atoms for which the Morse curves are not very accurate. Secondly, the calculated activation energy varies over a wide range for rather small changes in the division of the binding energy into its two parts. It is not surprising, therefore, that the calculated values are only in rough agreement with the experimental values. It must be noted, however, that calculations on a series of analogous reactions, for which a given set of assumptions holds with the same degree of validity, seem to yield the correct order for the reactivities. A third difficulty is that the possible interactions of two atoms cannot be represented by a single Morse curve. If all the data necessary for the calculation of all of the possible curves were available, this would not be a serious difficulty. Unfortunately, even for such simple and well-studied molecules as S_2 and I_2 , most of the data are not available. Hence there is no way of telling whether the discrepancies between the calculated and the experimental values of the activation energy originate in the first two difficulties, or whether the wrong Morse curve is being used. It may be possible at some later date to make these calculations with reasonable precision; for the present it must be considered that the physical significance of an activation energy is probably correct but that the numerical calculations are essentially qualitative.¹⁰

5.3 Experimental problems in reaction kinetics. From an experimental standpoint the problems which arise in the study of the kinetics of a photochemical reaction may be divided into two groups: (1) the determination of the rate law for the overall reaction; (2) the study of the rates of the steps assumed as the mechanism of a complex reaction. In the first case, it is necessary to determine both the form of the rate law and the magnitude of the rate. In the second,

¹⁰ For further applications of this method to the calculation of activation energies, the reader is referred to papers by Eyring and his students which have appeared beginning in 1931.

the rate law is the specific reaction rate multiplied by the product of the concentrations of the reactants. Thus, in the study of the hydrogen-chlorine reaction, the law for the rate of formation of hydrogen chloride had to be determined experimentally; but it was assumed that the rate of the reaction $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$, which is one of the steps in the mechanism, is given by $d(\text{HCl})/dt = k(\text{Cl})(\text{H}_2)$.

5.31 Determination of the overall rate law. The first step in the study of any reaction, whether or not it is photochemical, is to decide what reaction is being studied; i.e., what chemical equation expresses the change in composition of the system. There are many cases in which no one equation can be written because the reactive substances enter into two or more independent reactions. In the chapters on photolysis, many examples are cited in which the photo-activated molecule decomposes to give at least two sets of products. As an example we may cite N_2O , which decomposes to give N_2 , NO , and O_2 , a fact which is best represented by the two equations



Sometimes investigators have reported rates for such systems in terms of the rate of disappearance of the reactant. Although such data are often useful, from the standpoint of reaction mechanisms it is more important to know the factors which affect the composition of the products. Fortunately there are many systems in which only one net reaction occurs or in which, under certain limiting conditions, one net reaction can be written. These are the systems for which an overall rate equation is of value in determining the mechanism of the reaction. The only completely satisfactory evidence that the correct equation has been written is an analysis of the products which shows that the stoichiometric requirements of that equation are fulfilled.¹¹

¹¹ What constitutes an adequate analysis must be decided for each particular case. Sometimes it is sufficient to run the reaction until it is complete and then to analyze; other times, the system must be analyzed at various degrees of

Once the equation for the reaction to be studied has been established, any convenient method for following that reaction may be used to determine the rate law. If more than one reaction is occurring in the system, the best practice is to measure one of the products of the reaction to be studied. If only one reaction is occurring, a measure of the change of some physical characteristic of the system (such as pressure, light absorption, index of refraction, electrical conductivity, etc.) may be both satisfactory and convenient. Great care must be taken to ascertain that the measurement made really shows the extent of the reaction at the time. Many experiments which have been performed with great care have been misinterpreted or uninterpreted because it was assumed that the pressure change was proportional to the amount of reaction which had occurred. (Cf. §§ 8.32, 10.61.) In another case, the study of the replacement of bromine in CCl_3Br by chlorine, it was assumed in the early work that the reaction could be followed by the light absorption of bromine. Actually the product was BrCl and not Br_2 , and the difference in absorption is such that it introduced an error of a factor of ten in the reported rate. (Cf. § 11.53.)

With a definite reaction and a method of following it established, the rate should be studied as a function of the wave length, the concentrations of all the substances in the reaction mixture, the surface-volume ratio of the reaction vessel, and the total pressure in the case of gaseous systems. One of the most convenient methods for securing the data is to follow the variation in rate as only one factor varies. This may be accomplished by measuring initial rates for a series of reaction mixtures in which the concentrations of the constituents are varied one at a time. Another method is

completion of the reaction. For example, if the reaction between formaldehyde and chlorine is run until no further change in pressure occurs, the products are carbon monoxide and hydrogen chloride (if excess chlorine is present, the carbon monoxide reacts to form phosgene). However, in the course of the reaction a considerable amount of an intermediate, formyl chloride, is formed, and hence an analysis of a mixture in which the reaction is not complete would reveal a more complex situation.

to have all of the substances except one present at such concentrations that they are essentially constant, while the concentration of the one substance decreases to a small value.

Such data are then tested graphically, assuming various rate laws. If, at time t , x is the value of the concentration which is varying, the rate law is expressed as $-dx/dt = kx^n$. Here k includes the specific reaction rate and the values of the constant concentrations. It is readily shown that a straight line will be obtained by:

- (1) Plotting $\log x$ against t if $n = 1$.
- (2) Plotting $1/x$ against t if $n = 2$.
- (3) Plotting $1/x^2$ against t if $n = 3$.
- (4) Plotting $x^{1/2}$ against t if $n = 1/2$.
- (5) Plotting x^2 against t if $n = -1$.

The reaction is said to be of the first, second, or third order with respect to x if n equals 1, 2, or 3 respectively. This method tends to minimize experimental errors. If the graphical method is not used, it is a simple matter to observe whether doubling the value of x doubles, quadruples, etc., the rate. Other methods for determining the order of a reaction can be found in any text on physical chemistry.

In speaking about reactions, it may be well to distinguish at this point between the use of the terms *order* and *molecularity*. In the older literature the expressions *second order* and *bimolecular* were used interchangeably, but in recent years the term *order* has been restricted to the experimentally determined dependence of the reaction rate on the concentration. The terms involving molecularity, such as *unimolecular* and *bimolecular*, are used in speaking of the steps in a reaction mechanism. If only one molecule reacts in such a step, the reaction is unimolecular; if two react, it is bimolecular. Defined in this way, the order of a reaction is usually expressed by some small integral number or a very simple fraction, such as one-half. The number may be either positive or negative; i.e., the reaction rate may be either directly or inversely proportional to some power of

the concentration. On the other hand, the molecularity of a reaction is positive and limited to uni-, bi-, or ter- for all cases which have been studied.

Sometimes decimal orders such as 0.6 or 0.7 are reported for reactions. Usually it will be found that such statements are only approximations which hold over a limited range of concentrations. A more detailed investigation will show that the apparent order is the resultant obtained, for example, by adding two terms of different order, or by combining two terms in any way so that the rate is expressed by some function in which the concentration appears twice. Thus $x/(a + kx)$ may vary from proportionality to x to practical independence of x , depending on the values of x and the constants a and k . It is very important that the rate law should be expressed in the form which will hold over the widest range of conditions; hence, every effort should be made to eliminate odd decimal orders from the rate equations.

5.4 Mechanisms for reactions. Only in relatively few reactions are the final products formed as a direct consequence of the absorption of light. In most reaction mixtures the absorption of light produces reactive intermediates which enter into secondary reactions. The overall rate and the nature of the final products depend on the properties of these intermediates. It is an important task for the photochemist to determine the nature of these intermediates and the properties which determine the course of the reaction. The overall rate law is one of the facts which may be used for this purpose. In many photochemical reactions the rate is simply proportional to the rate of absorption of light. Under such conditions any information concerning the intermediates must be deduced from an analysis of the products, the quantum yield, and analogous or correlated reactions.

The problem of setting up a mechanism for a given reaction is one which should be approached with great caution since, in spite of the large amount of data in the literature, our knowledge of the properties of the atoms and radicals

which are the usual intermediates is extremely limited. Often it is possible to set up several mechanisms which will account equally well for the available data. The reasonableness of any particular mechanism must be judged on the basis of the probable chemical properties of the intermediates assumed and a comparison with other systems in which similar intermediates are assumed. In a sense, it is never possible to prove a mechanism unless all the steps can be isolated and studied separately. However, there are a number of reactions for which mechanisms have been devised which account for the experimental facts so well that the mechanisms are considered established.¹²

5.5 Kinetics of reactions involving atoms and radicals.

In most photochemical reactions the effect of the light absorption is to produce atoms or radicals. Hence a knowledge of the reactions of such particles is of particular importance for the interpretation of the secondary reactions which lead to the ultimate products. In particular, the recombination of atoms is of importance because it is the terminal step in any series of reactions initiated by the atoms.

The first reaction of this type to be studied directly was the recombination of hydrogen atoms. This reaction may proceed in the gas phase or on the walls of the reaction vessel. The homogeneous reaction has been studied quantitatively by several investigators.¹³ Although the experimental conditions and methods used were quite different, the result obtained in all the studies was that every collision between two hydrogen atoms in the presence of some third molecule results in recombination. The third body is required in order to remove enough energy to stabilize the newly formed molecule. If no energy were removed in this

¹² Cf. the reaction between bromine and hydrogen, which apparently proceeds through the same mechanism in the thermal and photochemical reactions, § 11.2.

¹³ Smallwood, *J. Am. Chem. Soc.*, **51**, 1985 (1929); Senftleben and Rieche-meier, *Ann. Physik*, **6**, 105 (1930); Steiner, *Z. physik. Chem.*, **B15**, 249 (1932); Farkas and Sachsse, *Z. physik. Chem.*, **B27**, 111 (1934); Amdur and Robinson, *J. Am. Chem. Soc.*, **55**, 1395, 2616 (1933).

way, the molecule formed as the two atoms approach would have sufficient energy in its one vibrational degree of freedom to dissociate in the second half of the first vibration. The heterogeneous reaction is not capable of such quantitative study, since the rate depends to a marked degree on the nature of the surface and its previous treatment. It was found in the first experiments with hydrogen atoms that dry glass or quartz surfaces are very much more effective in causing recombination than surfaces which have not been dried.¹⁴ Metallic surfaces are extremely effective in causing the reaction.

The recombination of the halogen atoms has been studied even more quantitatively than that of hydrogen atoms. In this case there is a possibility of stabilizing the quasi-molecule¹⁵ formed from one normal ($^2P_{3/2}$) and one excited ($^2P_{1/2}$) atom by radiation of light corresponding to the visible bands. Such a possibility does not need to be considered for hydrogen, as the first excitation of a hydrogen atom is so high (10.1 e.v.) that the fraction of collisions involving one atom in the higher state is negligible. Even with the halogens the number of atoms in the higher state at room temperature is too small to give a detectable effect. However, Kondratjew and Leipunsky¹⁶ have demonstrated that such a recombination does occur if a sufficient concentration of atoms in each state is present. The efficiency of the process is very low; they estimated that only one in 10^8 collisions of the proper type resulted in the emission of light. Since the mean life of the halogen molecules in the upper state for the visible bands is of the order of 10^{-8} sec. and the period of vibration of a diatomic molecule is usually estimated as of the order of 10^{-13} sec., it is readily estimated that the maximum efficiency which one could hope to find in such an experiment would be of the order of 10^{-5} . Actually it is never of importance in the study of any photochemical reaction.

¹⁴ R. W. Wood, *Phil. Mag.*, **42**, 729 (1921); **44**, 538 (1922).

¹⁵ The term *quasi-molecule* is often used in speaking of a molecule in a state in which it is unstable with respect to dissociation.

¹⁶ Kondratjew and Leipunsky, *Z. Physik*, **50**, 366 (1928).

The homogeneous recombination of halogen atoms by the triple collision mechanism has been studied extensively for bromine. Bodenstein and Lütkemeyer¹⁷ showed that a comparison of the thermal and the photochemical rates of formation of hydrogen bromide leads to the conclusion that at moderate pressures approximately one in eight hundred collisions between bromine atoms results in recombination. This is approximately the number of triple collisions under their experimental conditions. Jost and Jung¹⁸ extended these experiments over a wider range of total pressures and showed that the dependence of the rate of formation of hydrogen bromide on the total pressure is of the form required if the bromine atoms recombine according to the triple collision mechanism. Further experiments of this type were carried out by Ritchie and by Hilferding and Steiner¹⁹ with special reference to the efficiency of different gases as the third body. The results obtained are indicated in Table 8, which lists the rate

TABLE 8
RATE CONSTANT FOR $\text{Br} + \text{Br} + \text{M} \rightarrow \text{Br}_2 + \text{M}$

M	H ₂	He	A	N ₂	Br ₂	HBr	HCl	CO
$k \times 10^{-15}$	1.25	0.47	0.11	0.82	2.6	2.1	4.7	6.3

constant, k , for the reaction $\text{Br} + \text{Br} + \text{M} \rightarrow \text{Br}_2 + \text{M} +$ kinetic energy, as given by Hilferding and Steiner. The variation in efficiency is similar to that found for the quenching of fluorescence but is not so marked. It is to be noted that in this reaction, just as in the quenching of fluorescence, those molecules which can take up energy only as kinetic energy (i.e., He and A) are the least efficient.

Rabinowitch and Lehman²⁰ have studied the recombina-

¹⁷ Bodenstein and Lütkemeyer, *Z. physik. Chem.*, **114**, 208 (1925).

¹⁸ Jost and Jung, *Z. physik. Chem.*, **B3**, 83 (1929).

¹⁹ Ritchie, *Proc. Roy. Soc. (London)*, **A146**, 828 (1934); Hilferding and Steiner, *Z. physik. Chem.*, **B30**, 399 (1935).

²⁰ Rabinowitch and Lehman, *Trans. Faraday Soc.*, **31**, 689 (1937).

tion of bromine atoms in the absence of any other reaction. They determined the absorption by bromine molecules in the *photostationary state*²¹ set up by illumination with a carbon arc. The observed changes in absorption involve a combination of three effects, but at high pressures the main reaction is the triple collision recombination. Their figure for the rate constant using helium as the third body is 2.7×10^{15} , as compared to 0.47×10^{15} obtained by Hilferding and Steiner. The higher value is obtained by the more direct method and is probably more accurate.

The heterogeneous recombination of halogen atoms has also been noted. Hilferding and Steiner reported that the rate of the reaction on the walls depends on the previous treatment of the surface. Bodenstein and Winter,²² in their study of the hydrogen-chlorine reaction, concluded that only one in 6×10^3 collisions on silver chloride resulted in removal of a chlorine atom from the gas. A comparison of their quantum yields with values obtained in the presence of glass surfaces indicates that glass is about ten times as effective. The failure of the atoms to react at every collision with the surface does not seem to be due to the requirement of any heat of activation for the reaction, as no dependence on temperature has been noted. It must be attributed to a low efficiency of adsorption of the atoms on the wall.

The experimental facts which have been cited indicate that atoms unite to form a stable molecule at practically every collision in which a third body is present to remove some of the energy and to stabilize the molecule. A similar reaction is to be expected for the recombination of radicals, although in this case some inefficiency may exist on account of the requirement of a particular orientation of the groups for the reaction to occur. Since the molecules formed by the combination of two radicals are polyatomic and possess many degrees of freedom, it might be possible for two radicals to

²¹ The term *photostationary state* is used in speaking of a nonequilibrium state of a constant composition which is maintained by the absorption of light.

²² Bodenstein and Winter, *Sitzb. preuss. Akad. Wiss., Physik.-Math. Klasse I* (1936).

combine to form a quasi-molecule of rather long life because of a rapid distribution of the energy among the various degrees of freedom. Such a reaction may be looked upon as the reverse of a predissociation process. Furthermore, just as predissociation processes differ in probability, as shown by the variation in character of the spectrum, so must the probability of addition of two radicals vary with the nature of the radicals. If the predissociation process is slow (as indicated by a sharp or only slightly fuzzy spectrum), the recombination by the redistribution-of-energy mechanism must also be slow, and hence it will be negligible compared to a three-body mechanism. No experimental data have been presented which show such a bimolecular recombination.

Allen and Bawn²³ have recently shown that combination of two methyl radicals certainly requires more than ten collisions. Actually, some energy would eventually have to be removed or the molecule would predissociate; hence, an experimental effect which might be found is that abnormally large molecular diameters would be required to account for the observed rate by a termolecular mechanism. In effect, it might be said that two radicals could undergo a "sticky collision" which would increase the probability of losing energy to a third body.

That two radicals do combine has been demonstrated frequently. Leighton and Mortensen²⁴ found that in the photolysis of lead tetramethyl (cf. §8.9), which certainly involves methyl radicals, the products are lead and ethane. Spence and Wild,²⁵ in their study of the photolysis of acetone, found that above 60°C. the products are principally carbon monoxide and ethane (cf. §8.76). The ethane is believed to be formed by the combination of two methyl groups. Many other examples could be cited to show that two radicals do combine, but no details on the kinetics of the process are available.

Whether or not this type of reaction is of importance in

²³ Allen and Bawn, *Trans. Faraday Soc.*, **34**, 463 (1938).

²⁴ Leighton and Mortensen, *J. Am. Chem. Soc.*, **58**, 448 (1936).

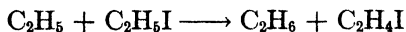
²⁵ Spence and Wild, *J. Chem. Soc.*, 352 (1937).

any given system depends to a large extent on the nature of the other molecules present. For example, although the mechanism of the decomposition of azomethane involves the formation of methyl radicals, the ethane found in the products is not formed by a direct combination of these radicals.²⁶ The radicals are removed by some more complex reactions with the other molecules present. It is not surprising to find such a situation since the radicals are present at much lower concentrations than the other molecules. If it is assumed that every triple collision involving two radicals results in combination and that the concentration of radicals is one-thousandth that of the other molecules, the activation energy for the reaction of the radical with the other molecule would have to be approximately 10 kcal. if the combination of radicals is to be important.

In addition to combination into a single molecule, there is the possibility that two radicals will react to form two molecules. Unfortunately, most of the reactions of this type which have appeared in the literature have been assumed in order to account for certain observations, but it is by no means certain that the assumption is correct. Thus two ethyl radicals may react according to the equation



Emschwiller²⁷ has stated that ethane and ethylene are formed in equivalent amounts under certain conditions in the photolysis of ethyl iodide. Although these products could be accounted for by the reaction just given, West and Schlessinger²⁸ suggest as an alternative mechanism



followed by the decomposition of $\text{C}_2\text{H}_4\text{I}$ into C_2H_4 and I .

In the later chapters, particularly Chapter VIII, various reactions of radicals with each other are written. Usually these are *ad hoc* hypotheses which have been introduced by various investigators in order to explain the results obtained

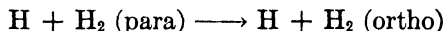
²⁶ Davis, Jahn, and Burton, *J. Am. Chem. Soc.*, **60**, 10 (1938).

²⁷ Emschwiller, *Ann. Chim.*, **17**, 413 (1932).

²⁸ West and Schlessinger, *J. Am. Chem. Soc.*, **60**, 961 (1938).

by them in the study of complex systems. It is often difficult to make a decision as to the validity of any particular assumed set of reactions which are self-consistent. However, the work of Leighton and Mortensen and of Spence and Wild is very strongly in favor of the view that the only reaction between two methyl radicals is the formation of ethane. Similarly, the preponderance of saturated hydrocarbons in the products found by Norrish and Appleyard²⁹ in the decomposition of methyl ethyl ketone suggests that, in a mixture of ethyl and methyl radicals, the simple addition of two radicals preponderates over any other type of reaction at ordinary temperatures. We should expect that the addition reaction would require little, if any, activation energy; on the other hand, the disproportionation reaction involves the breaking of a bond and therefore may be expected to have an appreciable activation energy. Only a few kilocalories difference in activation energy is sufficient to make one reaction negligible compared to another, if they both involve the same molecules.

5.6 Reactions of atoms and radicals with other molecules. Most of the information concerning the reactions of atoms and radicals with other molecules is indirect and depends on the validity of the assumptions used in connection with a complex mechanism. The reactions of atomic hydrogen have been studied rather extensively, usually by flow methods, since the atoms are most conveniently prepared by an electric discharge. The reaction of atomic hydrogen with molecular hydrogen was studied by A. Farkas³⁰ and by Geib and Harteck³¹ by introducing atomic hydrogen into para hydrogen and determining the amount of hydrogen converted to the ortho form.



The latter authors estimated the activation energy for the reaction to be ~ 7 kcal. This reaction has been used

²⁹ Norrish and Appleyard, *J. Chem. Soc.*, **874** (1934).

³⁰ A. Farkas, *Z. physik. Chem.*, **B10**, 419 (1930).

³¹ Geib and Harteck, *Z. physik. Chem.*, Bodenstein-Festband, 849 (1931).

extensively as a means of determining the concentration of atomic hydrogen in reaction mixtures. Such a test is not unambiguous, as the transformation of para to ortho hydrogen is brought about by any molecule or radical which contains an unpaired electron.³² The test also fails if the atomic hydrogen or other odd molecule is removed by some reaction with a lower activation energy than 7 kcal.

Atomic hydrogen reacts readily with oxygen, yielding water as the ultimate product; however, if the reaction mixture is cooled with liquid air at the point where the hydrogen and oxygen are mixed, a high percentage of hydrogen peroxide is formed.³³ This reaction has also been studied with atoms produced by the action of activated mercury atoms on hydrogen (cf. § 10.32). Bodenstein and Schenk concluded, from their study of the effect of oxygen on the hydrogen-chlorine reaction, that the reaction $\text{H} + \text{O}_2 \rightarrow \text{HO}_2$ requires an activation energy of ~ 1.5 kcal.³⁴

All the reactions of atomic hydrogen with the halogens and hydrogen halides are extremely rapid. Bodenstein and Jung³⁵ state that the ratio of the rate with Br_2 to that with HBr is 8.6 and is independent of temperature over a very wide range. The latter fact shows that there is no appreciable difference between the activation energies, both probably being zero.

Frankenburger³⁶ has shown that atomic hydrogen reacts with carbon monoxide to give formaldehyde and glyoxal. The experiments do not indicate the efficiency of the reaction, but the activation energy cannot be very high, as the reaction with CO occurs in preference to the recombination.

Bonhoeffer and Harteck³⁷ showed that the reactions of atomic hydrogen with hydrocarbons could be divided into three classes:

³² See § 5.91.

³³ Geib and Harteck, *Ber.*, **65**, 1551 (1932).

³⁴ Bodenstein and Schenk, *Z. physik. Chem.*, **B20**, 420 (1933).

³⁵ Bodenstein and Jung, *Z. physik. Chem.*, **121**, 127 (1926).

³⁶ Frankenburger, *Z. Elektrochem.*, **36**, 757 (1930).

³⁷ Bonhoeffer and Harteck, *Z. physik. Chem.*, **A139**, 64 (1928).

- (1) Dehydrogenating: $C_nH_m + H \longrightarrow C_nH_{m-1} + H_2$
- (2) Hydrogenating: $C_nH_{2n} + H \longrightarrow C_nH_{2n+1}$
- (3) Splitting: $C_2H_6 + H \longrightarrow CH_4 + CH_3$

These are followed by secondary reactions; hence, any conclusions concerning the characteristics of the primary steps are dependent on the assumptions made concerning these secondary steps. A very detailed study of the reactions of both atomic hydrogen and atomic deuterium with the aliphatic hydrocarbons has been made recently by H. S. Taylor and his associates.³⁸ They discussed the reaction mechanisms in considerable detail and presented a number of conclusions concerning possible activation energies for the reactions involved. (Cf. Table 33, Appendix III.)

The electric discharge has been used to prepare oxygen atoms, chlorine atoms, and hydroxyl radicals in order to study the reactions of these substances. The preparation of oxygen atoms is complicated by the formation of ozone, and in every case the calculation of the reaction efficiency is indirect. The formation of ozone is discussed later (§ 12.3). Chlorine atoms prepared in this manner were used by Rodebush and Klingelhoefer³⁹ to determine the activation energy of the reaction with hydrogen (~ 6 kcal.). Hydroxyl radicals have been prepared by the electrodeless discharge in water vapor. The reactions which follow the production of the radicals have been studied in detail by Rodebush, Wende, and Campbell⁴⁰ and by Oldenberg.⁴¹ The principal homogeneous reaction appears to be $H + OH + M \rightarrow H_2O + M$. These reactions are discussed in greater detail in a later section (§ 10.32).

The reactions of the alkyl radicals with normal molecules have been studied in many mixtures. Mention of the catalysis of the change of para into ortho hydrogen has already

³⁸ Trenner, Morikawa, and Taylor, *J. Chem. Phys.*, **5**, 203 (1937); Morikawa, Benedict, and Taylor, *ibid.*, **5**, 212 (1937).

³⁹ Rodebush and Klingelhoefer, *J. Am. Chem. Soc.*, **55**, 130 (1933).

⁴⁰ Rodebush, Wende, and Campbell, *J. Am. Chem. Soc.*, **59**, 1924 (1937).

⁴¹ Oldenberg, *J. Phys. Chem.*, **41**, 293 (1937).

been made. Leermakers⁴² has shown that the methyl radicals produced in the photolysis of acetaldehyde cause many additional molecules of the aldehyde to decompose. The low quantum yield of the photolysis of the alkyl halides is attributed to a high efficiency of the back reaction between the alkyl radicals and halogen atoms or molecules (cf. §8.2). Bates and Spence⁴³ showed that the photo-oxidation of methyl iodide to formaldehyde and iodine is in accord with the assumption that the molecules are split into CH_3 and I and that the CH_3 then reacts with oxygen. Reactions of methyl radicals with hydrocarbons or hydrocarbon derivatives, forming methane and leaving the other molecule deficient in hydrogen, have often been assumed. In general, it may be said that the free radicals are as reactive as might be expected from the fact that they contain an odd number of electrons. If the reaction is exothermic, it usually proceeds with a rather small heat of activation. Since the characteristics of any particular reaction of a radical are determined as a step in the study of some more complex reaction, the reader is referred for further details to such discussions (particularly in Chapter VIII) and to the table of activation energies (Table 33, Appendix III).

5.7 Budde effect and Draper effect. In gaseous systems two types of pressure increase have been observed which are in a sense dependent on rates. The Budde effect is an increase in pressure which occurs when some substance such as bromine vapor is illuminated. It is caused by the conversion of the absorbed energy into heat. In the case of bromine this occurs, at least partially, through the recombination of atoms in a triple-collision mechanism. There is no net reaction. The Draper effect is also a pressure increase and is usually associated with chain reactions, such as the hydrogen-chlorine and phosgene reactions. It is due to a warming of the reaction mixture by the heat liberated by the reaction; the more exothermic or the faster the reaction, the greater will be the effect. Neither phenomenon is of great

⁴² Leermakers, *J. Am. Chem. Soc.*, **56**, 1537 (1934).

⁴³ Bates and Spence, *J. Am. Chem. Soc.*, **53**, 381 (1931).

importance in photochemistry. If a reaction is being followed by change of pressure, it is necessary to eliminate the Draper effect from the measurements. Obviously, if the reaction rate is appreciably affected by temperature, it must be studied under conditions such that the Draper effect is negligible, for a large Draper effect indicates that the actual temperature of the reaction mixture is considerably above that of the thermostat in which the reaction vessel is placed.

5.8 Principle of microscopic reversibility. This principle has appeared in the literature under a variety of names. In addition to the name given here, it has been called the *law of detailed balancing* and the *law of complete chemical equilibrium*. This principle states that, in any system which is in equilibrium, the number of molecules changing from the initial to the final state by any one path is equal to the number changing from that final state back to the initial state by the reverse of that same path. It is to be noted that, according to this principle, it is not sufficient for the existence of an equilibrium to have the sum of the forward rates by all paths equal to the sum of the reverse rates.

The principle has already been used in § 3.22. It may be used also as a guide in deciding between possible reactions. For example, consider the possibilities represented by the equations



The compound AB is assumed to be the active intermediate which decomposes into the final products.⁴⁴ At equilibrium, the rate at which AB decomposes into the products is equal to the rate at which it is formed from those products. Now the reaction between E and 2F is termolecular, whereas that between C and D is bimolecular. Termolecular reactions are much slower than bimolecular; hence we may conclude that the decomposition into C and D is more

⁴⁴ In this discussion it is immaterial whether or not AB exists at appreciable concentrations.

probable than that into E and 2F. These considerations hold only if the activation energies are equal. If the decomposition into three molecules happens to have a lower activation energy than that into two molecules, then the former might be favored. Usually the decomposition into the larger number of molecules has the higher activation energy, since more bonds must be broken and fewer are formed. It is generally best to select the simplest types of reactions in setting up mechanisms.

5.9 General considerations concerning the rate of the overall reaction and the selection of a mechanism. It has already been said that the rate of the primary process in a photochemical reaction is proportional to the intensity of the light absorbed. The rate of the overall reaction is not determined by this factor alone. Usually the rate of one step in the mechanism can be written as the rate of formation of the products. This step involves a reactive intermediate which is formed, either directly or by way of some simple processes, by the action of light on the light-sensitive substance. If the permanent removal of this intermediate (i.e., the chain-breaking step) depends on a bimolecular reaction involving another such particle, then the overall rate will be proportional, not to the light absorbed, but to the square root of that quantity. On the other hand, if the removal of the reactive intermediates involves only one molecule of the intermediate, the overall rate is proportional to the rate of absorption of light.

Many studies have been made of the effect of change of wave length on the quantum yield and hence on the overall rate. If the rate depends on the square root, or any other than the first power of the light absorbed, the quantum yield depends on the light intensity. Hence, in order to detect any effect due solely to a change of wave length, the quantum yields at different frequencies should be compared at equal rates of absorption of light. If the comparison is made under such conditions (or if a correction is calculated), no effect will be observed when the primary step is a simple rupture of the absorbing molecule. The only possible effect

that could exist would be due to the increase in kinetic energy of the separating parts as the absorbed frequency is increased, which might supply part of the activation energy required in the secondary steps. Actually there are no experimental data which absolutely require such an assumption. On the other hand, if predissociation or a competition between two or more reactions is involved in the primary step, the probability of the occurrence of a particular process may vary with wave length and thus introduce a corresponding variation of quantum yield (cf. the aldehydes, § 8.72; ND_3 , § 7.71).

The selection of the steps to follow the primary process in a reaction mechanism involves two types of energy consideration: (1) Is the reaction thermodynamically possible? (2) Is the activation energy low enough for the rate to be appreciable under the given experimental conditions? The first question may be answered by a consideration of the energy change in the assumed reaction. Any exothermic reaction can proceed, provided the necessary activation energy is available. An endothermic reaction, on the other hand, can proceed only if the available energy is equal to the activation energy of the forward reaction, which is equal to the sum of the activation energy for the reverse process and the energy increase ΔE of the reacting system. Practically, if the endothermicity of the reaction exceeds a few kilocalories, the reaction will not proceed at room temperature. The magnitude of the activation energy for any step in a mechanism must be determined experimentally. If the same or a very similar reaction is used in another mechanism, an estimate of the required energy may be obtained from such a corresponding step.

The free energy change ΔF for a step is also frequently useful. According to thermodynamics,⁴⁵ $\Delta F^\circ = -RT \ln K$. It is readily shown, from the kinetic picture of equilibrium in a simple reaction, that the equilibrium constant K is

⁴⁵ The notation is the same as employed in Lewis and Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill Book Co., Inc., New York, 1923.

equal to the ratio of the specific reaction rates for the direct and reverse reactions. Therefore, we may write:

$$\Delta F^\circ = -RT \ln K = -RT \ln \frac{k_1}{k_2}$$

With the aid of this equation and a knowledge of the concentrations of the reactants and products, it is possible to decide whether or not the reverse process needs to be considered. In making such estimates, it must be remembered that fast following reactions may keep the concentrations of the products of the first step far below their equilibrium concentrations.

5.91 Detection of free atoms and radicals. In the verification of any mechanism suggested for a photochemical process, a point of considerable interest is the determination of the nature of the particles formed in the primary act. If they are exclusively stable molecules, this fact will be reflected in the invariability of the products when analyses are conducted at various stages of decomposition. Of course, if there are parallel paths by which a molecule might decompose into stable products in the primary step (cf. *n*-butyraldehyde, § 8.72), this invariability will not necessarily continue under changed conditions of wave length or of temperature. Usually, however, the problem is simplified. Of two possible paths for a reaction, one may involve radicals or atoms, and the other stable molecules. In such a case, the effect of variation of percentage decomposition, wave length, pressure, temperature, and the size and nature of the containing vessel on the composition of the products is frequently an excellent clue to the primary mechanism.

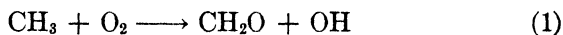
Analytical methods have been used rather successfully in this way by Leighton, Blacet, and their co-workers, in the study of the aldehydes (§ 8.72); by Norrish and his co-workers, on both aldehydes and ketones (§ 8.76); by Spence and Wild, on acetone (§ 8.76); by Fletcher and Rollefson,⁴⁶ in chain-reaction studies; and by Burton, Davis, and Taylor, on azomethane (§ 8.32). The principal

⁴⁶ Fletcher and Rollefson, *J. Am. Chem. Soc.*, **58**, 2129, 2135 (1936).

objection to analytical methods is that they are essentially indirect. They involve extrapolation from the analyses and the chemical properties of atoms and radicals to some frequently remote conclusions. The danger of the method may well be recognized from the statement that we still have much to learn about the reaction between two CH_3 radicals.

Other chemical methods are also frequently employed. For example, Patat (cf. §8.72) added oxygen to formaldehyde prior to photolysis, in order to detect free H atoms formed. Any such atoms would react with O_2 , yielding HO_2 and ultimately water. The formation of H_2O at $< 2750 \text{ \AA}$, but not above, was taken as an indication of the formation of H atoms only at shorter wave lengths. However, Caruthers and Norrish (cf. §11.6) obtained evidence for a chain photo-oxidation of HCHO under similar conditions, and consequently the method cannot be considered an unequivocal test, in this case at least.

Bates and his co-workers used the addition of oxygen as a test for free radicals in the photolysis of the alkyl halides (cf. §8.2). However, in the case of CH_3I , for example, where the reaction may be



the uncertainty of the method has long been recognized, and there has been persistent effort to verify the mechanism of the decomposition in other ways. West and Schlessinger have conducted the photolysis of the iodides in the presence of silver (cf. §8.2). In this case the increased quantum yield was attributed to the removal of iodine by the silver and the consequent prevention of a back reaction.

One of the most significant methods for the detection of free radicals and atoms is the *para-ortho hydrogen conversion* method of A. Farkas⁴⁷ and of Geib and Harteck.⁴⁸ This method depends on the fact that the equilibrium concentration ratio of ortho and para hydrogen at ordinary temperatures is 3 : 1. By exposure of hydrogen to activated char-

⁴⁷ A. Farkas, *Z. physik. Chem.*, **B10**, 419 (1930).

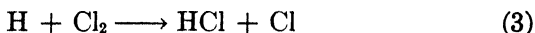
⁴⁸ Geib and Harteck, *ibid.*, Bodenstein-Festband, 849 (1931).

coal at liquid hydrogen temperatures, practically pure para H_2 may be formed.^{49a} At ordinary temperatures, conversion to the equilibrium ratio



occurs but slowly, except in the presence of a suitable catalyst. Such a catalyst may be a free hydrogen atom, an alkyl radical, or indeed any particle which contains an odd number of electrons or, for some other reason, is paramagnetic.^{49b, 50} NO, for example, catalyzes the conversion⁵¹ and the method has been used to prove the absence of paramagnetism in B_2H_6 , which cannot be studied by the ordinary method of measuring magnetic susceptibilities.⁵²

The disadvantages of this method for the detection of free radicals are twofold. In the first place, there is its catholicism. It detects anything which is paramagnetic and leaves the precise nature of the active particle to be determined by secondary evidence. Thus, we see that, although some particle formed in the photolysis of CH_3I catalyzes the conversion (§ 8.2), we cannot be certain as to its nature. It may be CH_3 , H , or I . In the second place, there is the difficulty of detecting such particles in the presence of any medium which removes them more quickly than $p\text{-}H_2$ itself can react to them. Thus, the method cannot be used in the ordinary way⁵³ for the detection of H atoms in the photochemical reaction between hydrogen and chlorine. Since the reaction



proceeds at room temperature at every 100th collision,⁵⁴ while reaction (4)



⁴⁹ (a) For details of preparation and testing, see A. Farkas, *Orthohydrogen, Parahydrogen and Heavy Hydrogen*, Cambridge University Press, 1935; (b) *ibid.*, p. 102.

⁵⁰ Cf. L. Farkas and Sachsse, *Z. physik. Chem.*, **B23**, 1 (1933); West, *J. Am. Chem. Soc.*, **57**, 1931 (1935).

⁵¹ L. Farkas and Garbatski, *J. Chem. Phys.*, **6**, 260 (1938).

⁵² L. Farkas and Sachsse, *Trans. Faraday Soc.*, **30**, 331 (1934).

⁵³ Bodenstein and Harteck, *Z. physik. Chem.*, **B4**, 113 (1929).

⁵⁴ Bodenstein, *Trans. Faraday Soc.*, **23**, 413 (1931).

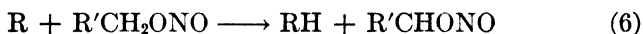
goes only at every $3 \cdot 10^6$ th collision, it is apparent that the method is applicable only if means are used to "protect" the H atoms.⁵⁵

Other methods for the detection of free radicals involve their removal by various chemical methods. Nitric oxide, for example, is supposed to react very readily with free radicals according to the reaction



If the free radical is CH_3 , the product would be expected to rearrange to give formaldoxime. No determination of the precise nature of the product has been reported, and consequently the assumptions involved in this method of testing cannot be considered verified. Nevertheless the method, which involves a study of the change of pressure or of rate during reactions with and without NO present, has proved helpful in studies by Thompson and Linnett, on mercury dimethyl (§8.9); and by Davis, Jahn, and Burton, on azomethane (§8.32).

Another reaction which may be used to remove free radicals has been more definitely established.⁵⁷ Methyl and ethyl nitrites react with free radicals according to the reactions



where R' is either H or CH_3 . Thus chains in which free radicals are the carriers may be interrupted by these reactions as well as by reaction (5). The relative merits of the two methods, and also of a method involving propylene, have been tested and discussed by Rice and Polley.⁵⁸ The nitrites are not particularly suitable in photochemical

⁵⁵ For a discussion of such a "protective" method, see Geib and Harteck, ref. 48; or A. Farkas, p. 103 of ref. 49.

⁵⁶ Staveland and Hinshelwood, *Proc. Roy. Soc. (London)*, **A154**, 335 (1936); *Nature*, **137**, 29 (1936); *J. Chem. Soc.*, 812 (1936).

⁵⁷ Cf. Rice and Rice, *The Aliphatic Free Radicals*, Johns Hopkins Press, Baltimore, 1935, p. 138.

⁵⁸ Rice and Polley, *J. Chem. Phys.*, **6**, 273 (1938).

studies because of the locations of their absorption spectra (§8.4) and of those of the product aldehydes (§8.71).

A notable contribution to the theory that free atoms and radicals are carriers of chains was made by Rice and Herzfeld,⁵⁹ and was tested by Allen and Sickman,⁶⁰ who sensitized the decomposition of acetaldehyde with free methyl radicals obtained from the pyrolysis of azomethane. Since that time, the reverse procedure has been followed. Substances which are believed to decompose via free radical chains are used as detectors of free radicals. For example, Leermakers studied the decomposition of dimethyl ether sensitized by free methyl radicals from acetone (§11.6). The method has been used extensively by H. S. Taylor and his co-workers.⁶¹

The most direct methods so far devised for the detection and identification of free radicals are the *mirror methods* devised by Paneth and developed by Rice and his co-workers. They depend on the fact that pure metallic (mirror) deposits of such elements as Pb, Sb, Hg, Te, etc. are readily removed by streaming gases known to contain free radicals. Lead, for example, reacts with free CH_3 according to the reaction



and it appears that every alkyl radical which strikes a clean Pb surface is fixed in this manner. The metallic alkyls thus formed may be collected and analyzed by micro-methods and the nature of the free radicals thus precisely determined. Also, indirect estimates may be made of their nature from their half-lives (determined from the time required for removal of the mirror deposit at different distances from the zone of decomposition). Such methods have been used with great success by Pearson and his co-workers in the study of the ketones (cf. § 8.76).

Prileshajeva and Terenin have employed photocells to

⁵⁹ Rice and Herzfeld, *J. Am. Chem. Soc.*, **56**, 284 (1934).

⁶⁰ Allen and Sickman, *ibid.*, **56**, 2031 (1934).

⁶¹ Cf. Taylor and Rosenblum, *J. Chem. Phys.*, **6**, 119 (1938).

measure the opacity of the mirrors.⁶² Leighton and Mortensen have used *radio-lead* (Ra-D) for more direct measurements.⁶³

Another variant on the mirror method is the guard mirror method devised by Burton.⁶⁴ In this method a lead mirror precedes an antimony mirror in the reaction tube. To sort out the free radicals and to detect the H atoms at the Sb mirror, advantage is taken of the fact that lead is insensitive to H atoms. The method has been used by Burton and Henkin in the study of the aliphatic acids (§ 8.8).

⁶² Prileshajeva and Terenin, *Trans. Faraday Soc.*, **31**, 1483 (1935).

⁶³ Leighton and Mortensen, *J. Am. Chem. Soc.*, **58**, 448 (1936).

⁶⁴ Burton, *ibid.*, **58**, 692, 1645 (1936).

CHAPTER VI

PHOTOLYSIS IN THE SOLID STATE

6.1 Order of discussion. Photodecomposition, or photolysis, is the first class of photochemical reaction considered, since a thorough understanding of the phenomena involved is frequently necessary to an appreciation and interpretation of other photochemical processes. As a matter of convenience, only the solid state will be considered in this chapter. The vapor state will be discussed in Chapters VII and VIII. The special aspects of the photochemistry of the liquid state are taken up in Chapter XIV.

6.2 Alkali halides in the solid state. The action of light on the alkali halide vapors produces no permanent, or net, effect because the products formed react much too readily with each other. In the crystal state, on the other hand, there is the possibility that the products once formed may be kept permanently at some distance from each other because of the effect of the lattice forces. That there is such a permanent effect may be seen in the case of ordinary rock-salt crystals, which become yellow on exposure to ultraviolet light.¹ Such crystals have to be heated to a high temperature if they are to be decolorized; they do not decolorize on standing. Thus it is apparent that, if methods are available for determining the number of color centers or *F* centers² formed and the number of quanta of light absorbed in the photochemical process, the quantum yield may be estimated. Such methods will be discussed in a later paragraph (§ 6.23). It is interesting that the solid state should provide one of the cases, unusual in photo-

¹ The coloration of glass in desert sunlight is due to a similar cause. This effect is not to be confused with the blue-violet color of sodium chloride crystals containing colloiddally dispersed sodium.

² The color centers receive the name *F* centers from the German *Farbzentren*.

chemistry, where a direct estimate of the quantum yield of the primary reaction is possible.

6.21 A model for the photochemical act. The photochemistry of the alkali halides has been associated with much

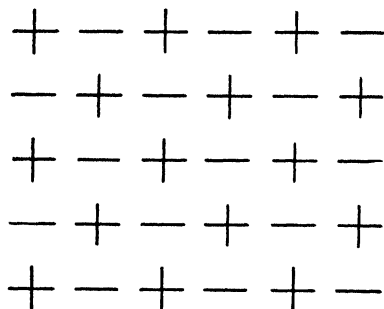


Fig. 16. Diagrammatic Representation of the Cross Section of an Alkali Halide Crystal.

confusion over a long period of years. It has been the unfortunate (although perhaps unavoidable) practice to collect data without concern about the correlation of such data with a reasonable model. For a review of some of the many experiments which have been performed, the reader is referred elsewhere.³ In this section we shall adopt the

somewhat unscientific device of describing what appears to be the most satisfactory model and of then interpreting the various observations in the light of that model. To be sure, this model may also have to be rejected on the basis of future discoveries. However, if it links together the present state of knowledge, it serves an admirable purpose. To relate the complete story of the other models would be more confusing than informative.

The cross section of any alkali halide in a plane containing halogen and alkali ions may be represented by a diagram such as is shown in Fig. 16, where the alternate halogen and alkali ions are represented by $-$ and $+$ signs respectively. It has been suggested by a number of investigators interested in this subject that,

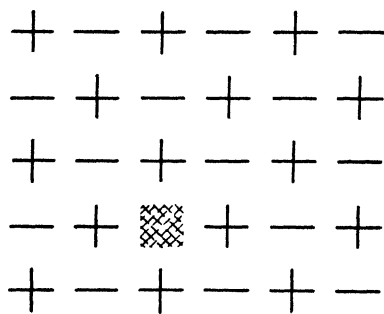
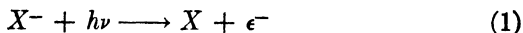


Fig. 17. Hole in a Crystal Lattice.

³ Pohl, *Proc. Phys. Soc.*, **49**, No. 274, 3 (1937).

even in an optically perfect crystal lattice,⁴ not all the points of the lattice are occupied by ions, but that there are empty spaces or holes in the crystal as shown in Fig. 17. Such holes are even in number. For every positive ion missing at one point, a negative ion is missing at another; the crystal as a whole is uncharged.⁵

If the alkali halide is designated as MX (where X is the halogen), then the favored model for the act of absorption is



where a free halogen atom (either in a normal or an excited state) and an electron are produced. This electron does not become associated with an alkali ion. Instead, it is free to wander through the "perforated" crystal⁶ until it comes to such a hole as is represented in Fig. 2, into which it sinks. In such a hole the electron is not associated with any particular alkali ion; neither is it free. Instead, it oscillates in the field of the six surrounding positive ions.⁷

The energy absorbed in the initial act corresponds to light (the normal or *N* spectrum) in the quartz or fluorite regions of the ultraviolet. In other words, the electron is bound rather firmly to the halogen ion. On the other hand, the "electron in a hole," the *F* center, is not so firmly bound. It has been mentioned that photochemically discolored rock-salt is yellow (i.e., it absorbs blue light). Similarly, it is found that all alkali halide crystals, once they contain *F* centers, thereafter absorb light in the near ultraviolet or the visible regions.

⁴ We are *not* referring now to so-called mosaic patterns. Cf. Leonhardt and Tiemeyer, *Z. Physik*, **102**, 781 (1936); Gogoberidze, *Physik. Z. Sowjetunion*, **11**, 621 (1937).

⁵ This model is due to deBoer. Cf. (a) deBoer, *Rec. Trav. Chim. Pays-Bas*, **56**, 301 (1937); (b) Mott, *Proc. Phys. Soc.*, **49**, No. 274, 36 (1937); (c) Mott and Littleton, *Trans. Faraday Soc.*, **34**, 485 (1938); (d) Mott, *ibid.*, **34**, 500 (1938); (e) Gurney and Mott, *ibid.*, **34**, 506 (1938).

⁶ Pohl, *Physik. Z.*, **35**, 107 (1934), has shown that the mean free path of electrons in halide crystals ranges from $\sim 10^{-6}$ cm. in NaCl to 1 cm. in AgCl crystals.

⁷ The correct quantum mechanical terminology would be that its wave function extends over the whole neighborhood of the six positive ions.

This absorption of light is associated with another photochemical act; the electron is extruded from the hole. When so extruded at a sufficiently high temperature,⁸ it may wander back to a halogen atom, which thereby becomes ionized; eventually, in this way, the crystal may be bleached of its color. On the other hand, it may wander to an unoccupied hole, into which it again sinks, and the net effect is zero. Or it may sink into a hole which already contains an electron; in this way two F centers are destroyed by one absorption act (with the formation of a new type, the F' center). Thus it is evident that the quantum yield of this photochemical act may vary from 0 to 2.0 under the most favorable conditions, whereas the primary act, by which the F centers are themselves produced, may have a maximum quantum yield of unity. "Two electrons in a hole" are called F' centers; they are both capable of light absorption and have the same absorption characteristics. Their light absorption regions lie about 2000 Å nearer the red. For potassium chloride, the first maximum in the N spectrum is near 1870 Å; its F maximum is at ~ 5400 Å, and its F' maximum is at ~ 7400 Å.

6.22 Normal absorption spectra of the alkali halides.

Studies of the absorption spectra of the alkali halides, both of crystals of extreme purity and of crystals to which impurities have been deliberately added, have been made principally by Hilsch and Pohl⁹ and by their collaborators at Göttingen.¹⁰ The investigations have been extended over a greater number of crystals and pushed farther into the extreme ultraviolet with brilliant success by Schneider and O'Bryan.¹¹ The

⁸ In the case of potassium bromide, this may occur at room temperature.

⁹ Hilsch and Pohl, *Z. Physik*, **57**, 145 (1929); **59**, 812 (1929); **64**, 606 (1930); **68**, 721 (1931); *Ber. VIIIth Internat. Congress of Photography, Dresden, 1931*, 29; *Nach. Ges. Wiss. Göttingen, Math.-physik. Klasse*, **1933**, 322, 406; *ibid.*, [N.F.] **1**, 115, 209 (1934). Pohl, *Naturwissenschaften*, **21**, 261 (1933); *Kolloid-Z.*, **71**, 257 (1935). Hilsch, *Angew. Chem.*, **49**, 69 (1936).

¹⁰ For an extensive bibliography, see Pohl, *Proc. Phys. Soc.*, **49**, No. 274, 3 (1937).

¹¹ Schneider and O'Bryan, *Phys. Rev.*, **51**, 293 (1937).

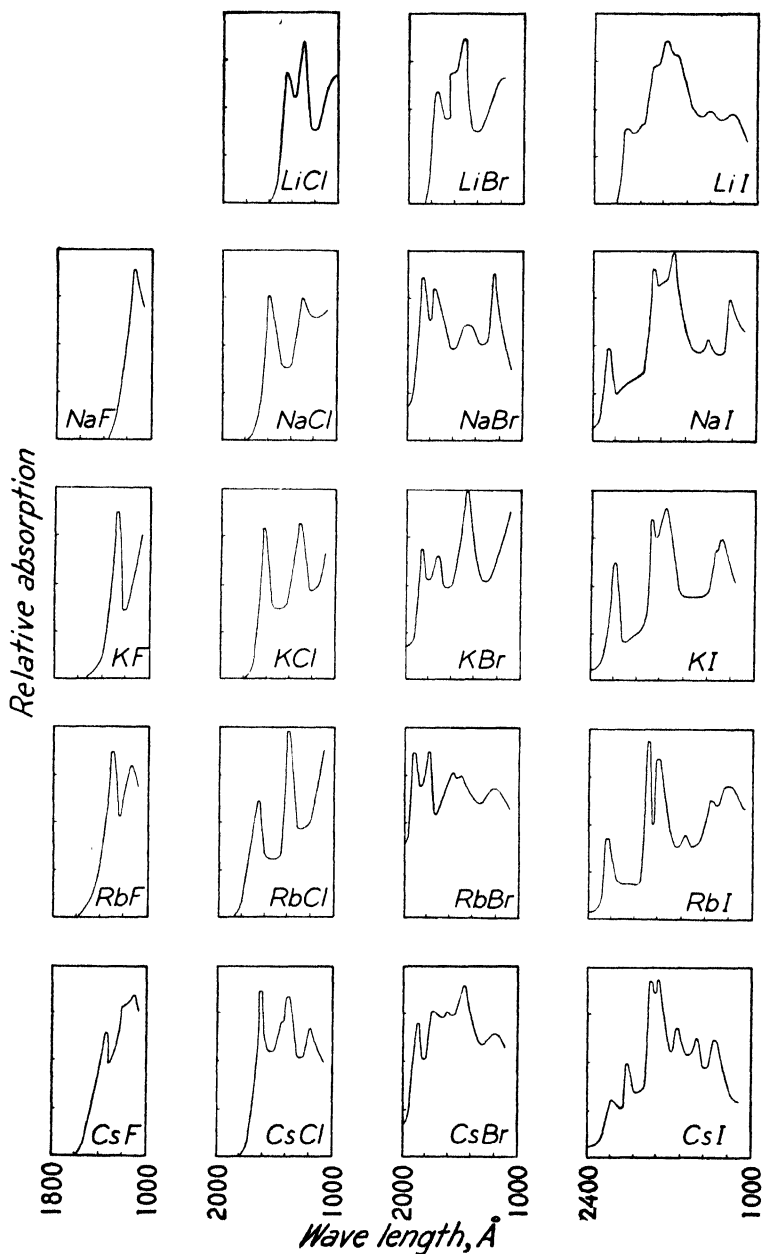


Fig. 18. Absorption Spectra of the Alkali Halide Crystals.

results of both groups are summarized compositely in Fig. 18.¹² (See p. 125.)

It is obvious that the positions of the absorption spectra and the locations of the principal maxima nearest the visible are determined primarily by the halogen ion. The effect of the alkali ion seems to be secondary. Lithium appears to have the greatest effect of any of the alkalis, all the lithium spectra being of shorter wave length than the other spectra of the corresponding halides. Recalling our model, we see that the first absorption maximum in each case (called the a maximum in Table 9) corresponds to the amount of energy required to convert a halogen ion to a halogen atom in the normal (unexcited) state within the lattice; i.e., the a maximum corresponds to the electron affinity of the halogen ions within the lattice. It may be seen from Table 9 that a averages ~ 6.5 volts for the bromides other than LiBr, or ~ 3 volts higher than the electron affinity of the Br^- ion in free space (3.53 volts). According to the model, it seems that one effect of the crystal lattice is to increase the electron affinity of the negative ion.¹³

If a corresponds to the energy required to leave the halogen atom in a normal state, then there should exist another maximum, a' , corresponding to the amount of energy required to leave the atom in the first excited state. The difference $a' - a$ would then correspond to the difference ${}^2P_{1/2} - {}^2P_{3/2}$, which are the first excited and the normal states of the halogen atom respectively. Such, in fact, is the case. The degree of agreement, as shown in Table 9, is remarkably good.^{13a} Better agreement cannot be expected since the lattice forces have a very obvious effect on the

¹² Strictly speaking, the results should not be directly compared since Hilsch and Pohl worked with crystals prepared from melts, and Schneider and O'Bryan used evaporated films. Hilsch and Pohl, *Z. Physik*, **59**, 812 (1930), found a slight shift toward the violet for evaporated deposits. However, the general form of the curves is as given in Fig. 18.

¹³ Other models have been proposed to explain these a maxima. Cf. Born, *Z. Physik*, **79**, 62 (1932); Klemm, *ibid.*, **82**, 529 (1933); Fues, *ibid.*, **82**, 536 (1933); von Hippel, *ibid.*, **101**, 680 (1936). Cf. also Mott and co-workers, ref. 5.

^{13a} In the free state, the differences for I and Br are 0.937 and 0.454 volts, respectively.

TABLE 9

POSITIONS AND COMPARISONS OF THE ABSORPTION MAXIMA OF THE SOLID ALKALI HALIDES

(Values expressed in volts)

Crystal	Electron Affinity Halogen Ion	a	a'	b	b'	c	c'	d	$a' - a$	$b' - b$	Excitation Potential Alkali Atom	Ionization Potential Alkali Atom
LiI	3.22	5.82	6.74	6.26	7.00	7.34	8.80	10.26	.92	.74	1.84	5.363
NaI		5.39	6.58			7.26	8.77	10.11	1.19		2.1	5.12
KI		5.63	6.58		7.07		9.57		.95		1.6	4.318
RbI		5.55	6.55		6.85	7.91	9.21	10.26	1.00		1.6	4.159
CsI		5.63	6.50	5.99	6.97	8.39	9.48		.87	.98	1.4	3.87
LiBr	3.53	7.13	7.61	7.90					.48			
NaBr		6.50	7.10		8.52	9.85			.60			
KBr		6.58	7.14	7.96	8.45				.56	.49	—	—
RbBr		6.43	6.93		8.45	10.04			.50			
CsBr		6.62	7.10	7.70	8.45	10.31			.48	.75		
LiCl	3.75	8.63		9.52								
NaCl		7.85		9.65								
KCl		7.60		9.42							—	—
RbCl		7.40		8.93								
CsCl		7.57		8.52		9.01		10.37				

energy levels of the atoms. For example, reference to Fig. 18 shows that the lattice forces are sufficient to widen the absorption *lines* so that they appear to be *bands* about 0.3 volts in width. If the ordinary temperature phenomena within the lattice are sufficient to produce such effects, it is evident that the lattice forces may act slightly differently on the different energy levels.¹⁴

In the case of the chlorides, we are confronted with the fact that ${}^2P_{1/2} - {}^2P_{3/2}$ for Cl is only 0.1 volt. Inasmuch as the line widths in the crystal run about 0.3 volts, it is obviously impossible to resolve the a and a' maxima.¹⁵ The nearest maxima for the chlorides, according to Table 9, are of the order of 1 volt apart. They are ascribable, not to the ${}^2P$ difference, but to another cause—probably the perturbations discussed in the following paragraph.

The lattice forces within the crystal are evidently constantly varied locally by temperature effects. It is this variation which is responsible for line broadening. On the other hand, the lattice forces themselves tend to influence the motion of the electrons within the field of any ion or atom within the lattice. However, there is not a continuous variation of this effect. The lattice forces, in general, produce additional perturbed quantized energy levels in the atoms or molecules affected. This occurs generally, except in the case of P levels without spin in cubically symmetrical lattices.¹⁶ In a case such as this, where the atoms are produced with spin, it is possible that the ${}^2P$ final states may be perturbed into several quantized energy levels whether or not the initial state of the ion (presumably ${}^1S_0$) is so perturbed. Thus we see that, in this way, other lines besides the a and a' lines would logically be expected. An attempt at classification of these lines is made in Table 9. In accord-

¹⁴ It must be remembered, of course, that only the difference $a' - a$ corresponds to ${}^2P_{1/2} - {}^2P_{3/2}$. The ${}^2P$ states of the atom within the crystal lattice are probably different from the ${}^2P$ states in free space.

¹⁵ It would be interesting to perform experiments at liquid hydrogen temperatures; under these conditions, resolution of these lines and others might be expected.

¹⁶ Cf. Bethe, *Ann. Physik*, **3**, 133 (1929).

ance with what might be expected from the concept of perturbed upper states, some of these secondary lines (the b lines in LiI and CsI) actually fall lower than the a' lines. The model which would allow for perturbations of the upper levels has been used, in a general way, to account for the multitude of maxima in the crystals of the alkali halides.¹⁷ However, much theoretical as well as experimental work remains to be done before this phase of the problem may be considered completed.

6.23 Production of F centers. It has previously been stated (in § 6.2) that, when alkali halide crystals are illuminated in the ultraviolet in the region of their normal absorption spectra, colored crystals are obtained. It has been indicated (§ 6.21) that a satisfactory model for this process is the absorption of energy by a halogen ion with the extrusion of an electron which then wanders about in the "perforated" crystal lattice until it falls into a hole (where a negative ion is missing), whereupon it oscillates within the field of the six neighboring positive ions. Such an electron in a hole absorbs light in the near ultraviolet or the visible; this is the model for the F centers.¹⁸

Irrespective of the model, the color or F centers are, of course, a physical reality. Their production is the result of a photochemical change in the crystal, and the quantum yield can be measured, though not by the conventional chemical means. Smakula,¹⁹ for example, calculated from the intensity of the coloration the number of F centers formed. The results for potassium bromide are shown in Fig. 19 (p. 130). At lower percentages of "decomposition," the quantum yield approaches 1.0 as a limit.²⁰ It appears that the crystal tends to become saturated with F centers. This is not surprising for, according to the model, there is

¹⁷ For other models, cf. Hilsch and Pohl, *Z. Physik*, **59**, 812 (1929); von Hippel, *ibid.*, **93**, 86 (1934); Mott, ref. 5d.

¹⁸ Pohl has likened these F centers to the photographic *latent image* (see § 6.31).

¹⁹ Smakula, *Z. Physik*, **63**, 762 (1930).

²⁰ The quantum yield may be measured also by electrical means. Cf. Hilsch and Pohl, *Z. Physik*, **68**, 721 (1931).

only a finite number of "holes" available to be filled by free electrons. As the number of such holes remaining decreases, the possibility of the back reaction increases, with consequent reduction of the quantum yield. It is

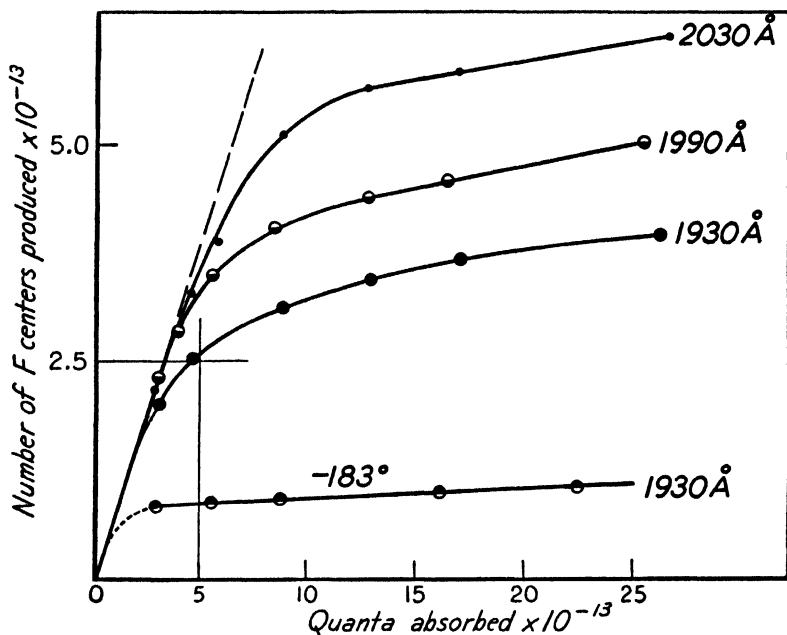


Fig. 19. Quantum Yields of the Production of F Centers in KBr at various temperatures as a function of light absorbed.

interesting that the greatest yield per absorbed quantum is attained, according to Smakula, not at the absorption maximum but at the beginning of the continuum and that decreasing the temperature also decreases the yield. The model of the "perforated" crystal fails to explain this result, although it does in a way explain the following: the greater the amount of impurity and other lattice disturbances (e.g., cracks, breakage, strains, etc.), the nearer has the quantum yield approached to unity.²¹

²¹ Cf. Smekal, *Ber. VIIIth Internat. Congress of Photography, Dresden, 1931*, 34. Attention should also be called to the extended chapter by Smekal, "Strukturempfindliche Eigenschaften der Kristalle," in *Handbuch der Physik*, 24, 795-922, Julius Springer, Berlin, (2nd ed.) 1933, which contains some very interesting information pertinent to this whole subject and many references.

F centers may also be produced by exposing the crystals to alkali vapor at high temperature and then suddenly quenching them,²² or by introducing electrons into a hot crystal from a pointed cathode.²³ In the latter case, halogen is simultaneously ejected.⁶ According to the "perforated" crystal model, the explanation of the former method is simply that alkali atoms enter the crystal and become ionized, the alkali ions entering holes in the neighborhood of negative ions and the electrons entering holes in the neighborhood of positive ions and thus forming F centers. Presumably, when the F centers are produced by forcing electrons into the crystal, the electrons simply occupy the holes left by the halogen ions which they displace. The latter are then neutralized outside of the crystal or at the anode.

Another method for the production of F centers may seem somewhat the reverse of that described above. A colored crystal (i.e., one containing F centers) is prepared with alkali vapor as just indicated. It is then heated in hydrogen, and the color disappears. Study of this crystal in the ultra-violet shows that a new absorption band has developed, somewhat nearer the visible. These bands are called U bands; they are really the absorption spectrum of alkali hydride dispersed in the alkali halide crystal.²⁴ When such crystals are illuminated in their U -band region at sufficiently high temperature, the U centers are converted to F centers with a quantum yield approaching unity.²⁵ Mott⁶ has given a picture which fits this phenomenon to the perforated lattice model.

²² Ottmer, *Z. Physik*, **46**, 798 (1928); Pohl, *Kolloid-Z.*, **71**, 257 (1934). Mollwo, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse, Fachgruppen II*, [N.F.] **1**, 215 (1935), also prepared " K centers" by introduction of halogen into the crystal.

²³ (a) Pohl, *Naturwissenschaften*, **20**, 932 (1932); (b) **21**, 261 (1933).

²⁴ At one time it was thought that U centers arose from the alkali metal itself. In referring to the earlier literature, the reader must remember that these U centers are hydrides. Cf. Hilsch and Pohl, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse, Fachgruppen II*, [N.F.] **2**, 139 (1936).

²⁵ Hilsch and Pohl, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, **1933**, 406; [N.F.] **1**, 115 (1934).

It was found by Helbig²⁶ that plastic deformation shifted the F maxima toward longer wave lengths. The results of Mollwo,²⁷ who found that they were similarly shifted by an increase of temperature, may be considered to be of a similar nature, for increase of temperature likewise puts a strain on the lattice forces. The reality of these forces may also be judged from the work of Podashevskii,²⁸ who studied the effect of ultraviolet light and of x-rays on the elasticity and rigidity of rock-salt crystals. He found that the effects of both radiations were identical, that the rigidity was increased an average of 143.3 per cent and the elastic limit 75.6 per cent by irradiation of the crystal.

6.24 Production of F' centers. When a crystal containing F centers is illuminated in the region of its F maximum at sufficiently low temperatures,²⁹ new absorption maxima about 2000 Å further toward the red are produced. The centers responsible for this absorption are called F' centers. According to the perforated lattice model (§ 6.21), an F center absorbs light and thereby the electron is extruded from its hole. If it wanders about until it enters a hole already containing an F center, we then have two electrons in a hole; i.e., two F' centers, which have similar energy states and are less firmly bound to the six neighboring positive ions than are the F centers. This model agrees with the fact that the limiting quantum yield of production of F' centers from F centers is 2.0, for in this way two F' centers are formed for each absorption act. At higher temperatures the quantum yield is reduced by the reverse action $F' \rightarrow F$, as well as by the tendency for F centers to revert to conditions of the normal crystal.³⁰

6.25 Problems in the photolysis of alkali halides. Not all of the problems suggested by the photochemistry of the

²⁶ Helbig, *Z. Physik*, **91**, 573 (1934).

²⁷ Mollwo, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, **1931**, 97, 236. Mollwo also noted that, for different crystals, the frequencies of the F maxima are proportional to the squares of the lattice constants.

²⁸ Podashevskii, *Physik. Z. Sowjetunion*, **8**, 81 (1935).

²⁹ Gyulai, *Z. Physik*, **33**, 251 (1925); **46**, 80 (1927). Hilsch and Pohl, *ibid.*, **68**, 721 (1931). Pick, *Ann. Physik*, [5] **31**, 365 (1938).

³⁰ Gudden and Pohl, *Z. Physik*, **31**, 651 (1925).

alkali halide crystals are cleared up by the perforated lattice model. Some new ones are introduced, and for others the model requires clarification. In this connection the reader is referred to the literature for further information about the $U \rightarrow F$ transition and the suggested model. Furthermore, as long as the model remains purely qualitative, it cannot be considered eminently successful. Satisfactory calculations of the α , α' , and other maxima are still to be made.^{5d,e} Neither is there in the model anything which explains why, for potassium bromide (see Fig. 19), the maximum quantum yield of F -center production is obtained at the beginning of the continuum or why low temperature decreases the quantum yield.

6.3 Silver halides in the solid state. In any discussion of the silver halides it is necessary to delimit the subject matter sharply to avoid attempting to cover the whole field of photography. In this section, we shall consider the silver halides in the macroscopic crystal state; in the chapter on heterogeneous systems, we shall take up the subject again (§15.3), paying special attention at that time to the effect of particle size, the effect of the supporting medium, and the effect of sensitizers.

6.31 A model for the photochemistry of the silver halides. It has long been recognized that the photochemistry of the silver halides is similar to that of the alkali halides.³¹ In recognition of that similarity, Pohl^{23b} has likened the F centers produced in the photolysis of the latter to the *latent image* in photography (see § 6.23). In both cases the primary act consists in the absorption of light in a halide ion, followed by separation of an electron from that ion and its movement to some other point in the crystal. It has been shown that a satisfactory model for what occurs is the assumption that the electron finally enters a "hole" in the lattice (see § 6.21), where it then proceeds to oscillate in the neighborhood of the six neighboring positive ions. However, in the silver halides the mean free path of the

³¹ Cf. Goldstein, *Z. Instrumentenkunde*, **16**, 211 (1896).

electron is much greater ⁷ and there is consequently a great probability that the electron will reach a disturbed portion of the crystal (i.e., a surface crack, flaw, or impurity) where it may discharge a silver ion and form an atom.

According to Pohl, the *F*-center picture is a good description of the latent image.³² The only reason that the latent image of photography is invisible is because the crystals in the photographic plate are extremely small. Working with a thick AgBr crystal, Pohl was able to produce a blue coloration. On the other hand, Löhle³³ found that the photochemical reaction products in crystals of silver chloride show absorption bands which must be due to flocculated particles. However, the results of Pohl and of Löhle are not necessarily contradictory. Although Savost'yanova³⁴ showed that, even in crystals, the particles of silver in the latent image may be at least 30 μ in diameter, there is good reason to believe that *F* centers may exist simultaneously with or prior to the formation of such particles. Tammann and Bandel³⁵ found that, when the silver halide crystals are distorted *after* exposure to light, ultramicroscopic examination shows that agglomerates of silver are formed in the planes of fracture. An obvious conclusion is that a latent image of the type postulated by Pohl, consisting of *F* centers (i.e., electrons in "holes"), is produced in the crystal on illumination. The production of the larger particles is a secondary phenomenon which occurs simultaneously with the formation of *F* centers;³³ if such a crystal is subjected to disturbance after the formation of *F* centers, large particles are formed at the foci of disturbance. According to the perforated lattice model, these particles are formed merely by the migration of electrons to a locus of disturb-

³² In photography the latent image is an unseen, invisible image produced in the plate on exposure. It may be made visible by proper means (i.e., development) or practically destroyed by others (e.g., flooding with infrared light).

³³ Löhle, *Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, **1933**, 271.

³⁴ Savost'yanova, *Science ind. phot.*, **2**, 6, 285 (1935); *Chimie & industrie*, **35**, 380. Savost'yanova and Toporetz, *Compt. rend. acad. sci. (U.R.S.S.)*, **2**, 225 (in German, 228) (1934).

³⁵ Tammann and Bandel, *Z. anorg. allgem. Chem.*, **214**, 403 (1933).

ance, where they discharge a number of silver ions forming an aggregate. Löhle's work³³ indicates the improbability that such aggregates are formed by migration of atoms, for the size of the aggregates seems to be independent of the temperature at which they are formed or of the time between exposure and ultramicroscopic examination.

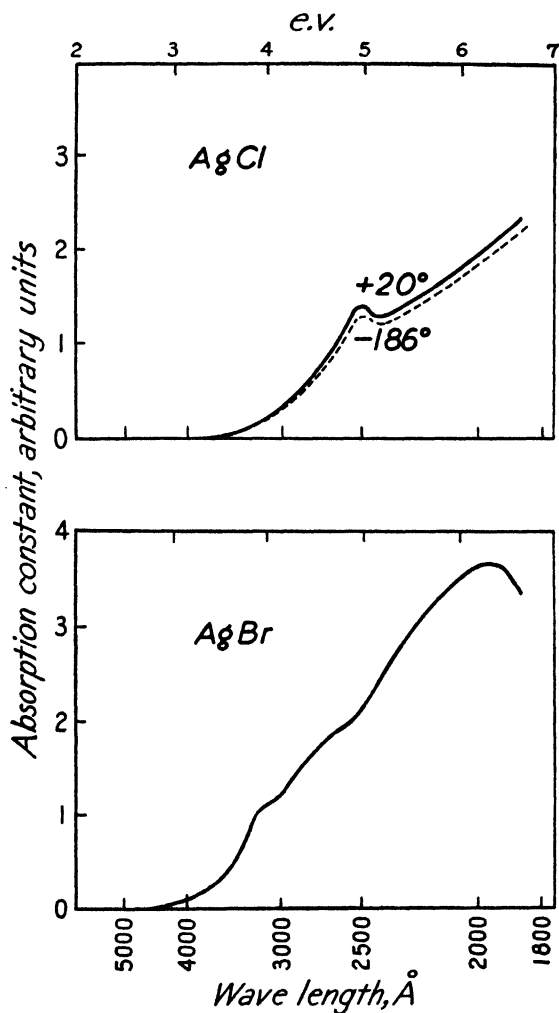


Fig. 20. Absorption Curves for Silver Halides, according to Hilsch and Pohl, *Z. Physik*, **64**, 606 (1930). The arbitrary unit is $\sim 10^6 \text{ cm.}^{-1}$

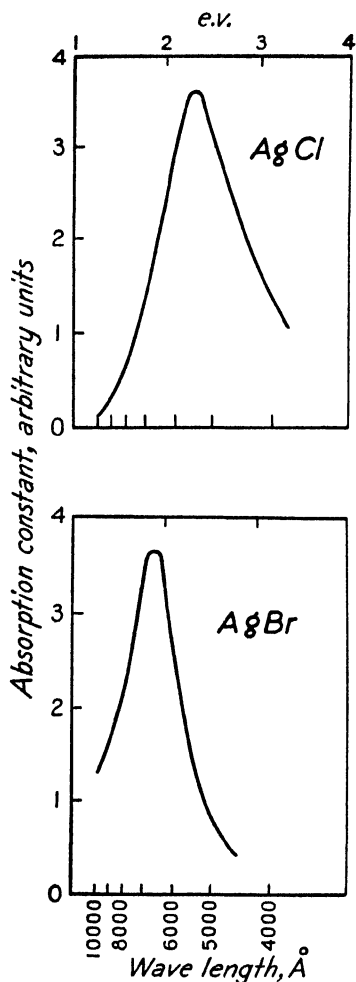


Fig. 21. Absorption Curves for "Discoloration" of Silver Halides, according to Hilsch and Pohl, *Z. Physik*, **64**, 606 (1930). The arbitrary unit is $\sim 1 \text{ cm.}^{-1}$; i.e., the ratio of the units in Figs. 20 and 21 is $10^6 : 1$.

6.32 Absorption spectra.

The silver halides differ from the alkali halides in the much wider range covered by their absorption spectra. Fig. 20 (page 135) shows that, whereas the absorption spectra of the alkali halides have sharp maxima and begin far in the ultraviolet ($\sim 2000 \text{ Å}$; see Fig. 18), those of silver chloride and silver bromide have very broad maxima and absorb even in the visible. The extinction coefficients are of the order of 10^6 cm.^{-1} and, as may be seen for silver chloride, are practically unaffected by changes in temperature extending from -186° to 20° . The absorption spectra of the "discolorations" in the silver halide crystals³⁶ are shown in Fig. 21. The extinction coefficients shown at the maxima are of the order of 1.0 cm.^{-1} . The number of F centers formed may be calculated from the intensity of the coloration.¹⁹

6.33 Quantum yield. It is possible in the way just described, by determining the number of quanta absorbed

³⁶ Hilsch and Pohl, *Z. Physik*, **77**, 421 (1932). V. Smakula, *ibid.*, **45**, 1 (1927), for the effect of dispersing silver halide in alkali halides; the spectra are shifted toward the ultraviolet.

in the process of photolysis and by determining the extinction coefficient at the absorption maximum in the region of the discoloration, to make a calculation of the quantum yield of discoloration, i.e., of the F centers, in the photolysis. The curves shown in Fig. 22 were obtained in this way.³⁷ The maximum quantum yield of silver atoms, at weak illumination, was about 0.33 for silver chloride and about 0.4 for silver bromide.³⁸ As in the case of the alkali chlorides (see §6.23), the quantum yield decreased with increasing intensity of illumination. It is likewise found that the quantum yield is improved in imperfect crystals. In the light of the perforated lattice model, the explanation appears obvious.

It may be seen that, as far as quantum yield in the absorb-

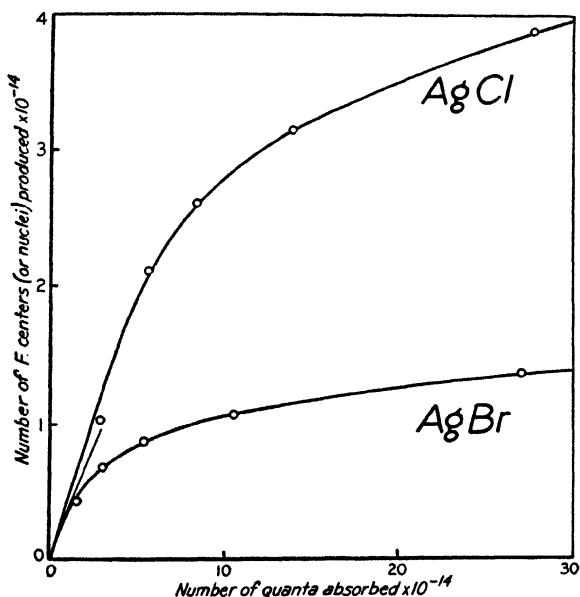


Fig 22. Quantum Yields in the Photolysis of Silver Halides, according to Hilsch and Pohl, *Z. Physik*, **64**, 606 (1930). AgCl layer 1.4 mm. thick, $\lambda = 4050 \text{ \AA}$. AgBr layer 1.8 mm. thick, $\lambda = 4750 \text{ \AA}$.

³⁷ Hilsch and Pohl, *ibid.*, **64**, 606 (1930).

³⁸ Hecht, *ibid.*, **77**, 235 (1932), on the other hand, reports quantum yields for silver chloride ranging from 0.34 to 0.58.

ing region is concerned, silver halide crystals are in no way superior to alkali halide crystals. Their photographic superiority resides in the more favorable position of their absorption spectra, the much greater stability of their products of photolysis, and the possibility of development.³⁹ In the crystal state the products are not absolutely stable; just as for the alkali halides, there are possibilities of regression or decay of the latent image.⁴⁰ We shall see later (§15.3) that it is part of the function of the emulsion in photography to fix the latent image.

Martens⁴¹ has made measurements of the quantum yield in silver bromide crystals, in which he made use of alteration in the dielectric constant on illumination. He found a quantum yield of 0.18. Chemical means for the determination of quantum yield will be mentioned in a later section (§15.31).

6.34 Problems in the photochemistry of silver halide crystals. There is an unfortunate tendency to consider a problem answered when a satisfactory model is found. We have seen in the case of the silver halides, that some stretching and pulling is necessary, if the perforated lattice model is to be made to fit the facts as they are now known. For example, we have tacitly assumed that, for every silver atom appearing in a particle agglomerate, an F center has disappeared. There does not appear to be any evidence for such a statement, although it is at least a convenient assumption. Experimental information on this point is highly desirable. Later, in a discussion of photography, we shall refer to a parallel question. The latent image is presumably invisible and developable into a visible image. Which is the developable latent image? Is it the F -center image? Is it the pattern of silver particles (aggregates of atoms)? Or, is it both? Photographic experience has in the past suggested that the silver particles are developable into an image; on the other hand, the work on the thallous

³⁹ Urbach, *Science ind. phot.*, **2**, 6, 288 (1935); *Chimie & industrie*, **35**, 380 (1935).

⁴⁰ Cf. Wulff, *Phot. Korr.*, **70**, 131 (1934).

⁴¹ Martens, *Z. Physik*, **103**, 217 (1936).

halides (see § 6.4) definitely suggests that the F centers play an important role. If the F centers are the developable centers, we have a convenient model to explain the process of development (see § 6.4), and also a very suggestive starting point for future technological advances.

There is also an extremely interesting problem in the absorption spectra, puzzling on its face: Why are the absorption "lines" of the silver halides so wide compared with those of the alkali halides?

6.4 Photolysis of some other crystal molecules. In Table 10 (p. 140) are data concerning some additional crystal molecules which have been photochemically investigated. Of the group, the thallous and the cuprous salts deserve special mention. In both cases investigators have concerned themselves with photographic possibilities and have obtained interesting results.

Farrer⁴² prepared emulsions with thallous bromide and concluded that they accept a latent image on exposure since, after treatment with silver nitrate, they can be developed and fixed in the same way as photographic plates. Photographs of sets of crystals before and after treatment with silver nitrate solution showed that the replacement of thallium by silver took place, as far as could be determined, without any alteration in crystal state or structure. Presumably, either we are here concerned with diffusion of the atoms in the crystal; or we are to make the more reasonable conclusion that, in thallous bromide as in the alkali halides (see § 6.21), F centers (i.e., electrons in lattice "holes") are formed and that the electrons concerned may diffuse to cracks, cleavage planes, and other foci of disturbance, where they may interact with silver ions to give the large particles characteristic of the ordinary photographic latent image.

Pavolini⁴³ prepared photographic emulsions containing cuprous chloride and cuprous bromide. He found that the principal difficulties attending the use of such salts were

⁴² Farrer, *Nature*, **137**, 276 (1936).

⁴³ Pavolini, *Corriere fot.*, **31**, 581, 637 (1934).

their poor keeping qualities, because of a tendency to oxidation, and the difficulty of obtaining a properly fixed image.

TABLE 10
PHOTOCHEMICAL STUDIES OF SOME SOLID SUBSTANCES

Substances	Wave Length	Effect	Reference
Alkali halides	See §§ 6.2 to 6.24.		
Silver halides	See §§ 6.3 to 6.34.		
Cuprous halides	See § 6.4		
Thallous halides	5350 Å See also § 6.4.	Resemble silver halides. <i>F</i> maximum for TiCl.	(1) (2)
Zinc sulfide	u.v.	Turns black.	(3), (10)
Cinnabar (Mercuric sulfide)	u.v.	Turns black without change of crystal form.	(4)
Magnesium oxide	2537 Å 4538 Å	Tinted deep purple. Decolorizes colored crystal in 30 minutes.	(5)
Lead suboxide	Blue-violet from quartz lamp.	Becomes brownish red in 10 hours; grayish brown in 50 hours.	(6)
Lead dioxide	Blue-violet from quartz lamp.	Becomes reddish brown.	(6)
K, Na, Sr, Ba, Cd, Al, Pb, and NH ₄ nitrates	2500 Å	Nitrite formed near surface; effect decreases in order given. Plane of polarization is important.	(7), (8)
Lithium hydride	2537 Å	H ₂ liberated. Crystals colored greenish blue. Low γ (5%) attributed to H stuck in lattice.	(9)
Hydrogen bromide	See § 7.81.		
Hydrogen iodide	See § 7.81.		

REFERENCES

- (1) Hilsch and Pohl, *Z. Physik*, **64**, 606 (1936).
- (2) Fesefeldt, *ibid.*, **64**, 741 (1936).
- (3) Platz and Schenk, *Angew. Chem.*, **49**, 822 (1936).
- (4) Brosset, *Naturwissenschaften*, **24**, 813 (1936).
- (5) Hibben, *Phys. Rev.*, **51**, 530 (1937).
- (6) Hoffman, *Z. anorg. allgem. Chem.*, **228**, 160 (1936).
- (7) Narayanswamy, *Trans. Faraday Soc.*, **31**, 1411 (1935).
- (8) Cf. Krishnan and Guha, *Proc. Indian Acad. Sci.*, **1A**, 242 (1934); *Current Sci.*, **2**, 476 (1934).
- (9) Bach and Bonhoeffer, *Z. physik. Chem.*, **B23**, 256 (1933).
- (10) Gloor, *Helv. Chim. Acta.*, **20**, 853 (1937); cf. Baur, *ibid.*, **20**, 878 (1937).

6.5 Effect of polarized light. In Table 10, reference was made to the photolysis of nitrate crystals, which on decomposition yield nitrite and oxygen. The nitrite is formed only near the surface, since the O atoms formed by decomposition in the interior cannot escape and recombination results. Narayanswamy⁴⁴ showed that polarized radiation, the vibrations of which are along the normal to the plane of the nitrate ions, is much less effective in dissociating the ions than radiation with vibrations in the plane of the ions.

A selective effect of polarized light is, of course, to be expected only when the substance affected is itself arranged in an orientated pattern. Thus, such an effect is not to be sought in liquids or gases, except in the theoretically conceivable case of molecules orientated under the influence of intense fields. Such conditions might exist, for example, in adsorbed liquid or gaseous layers. Similarly, photosensitive molecules may be orientated by the system in which they are suspended; e.g., some degree of orientation may be produced in an emulsion, and there may be, in consequence, a special sensitivity to one or another plane of polarized light.⁴⁵ It is sufficient to indicate the possibility of such phenomena; Narayanswamy's results show their actuality.⁴⁶

⁴⁴ Narayanswamy, *Trans. Faraday Soc.*, **31**, 1411 (1935).

⁴⁵ Cf. Cameron and A. M. Taylor, *J. Optical Soc. Am.*, **24**, 316 (1934).

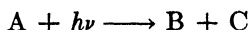
⁴⁶ Cf. Weigert, *Naturwissenschaften*, **3**, 583 (1921); **19**, 963 (1931). The effect of circularly polarized light is discussed in § 14.8.

CHAPTER VII

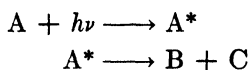
PHOTOLYSIS OF VAPORS OF INORGANIC COMPOUNDS

7.1 Classification. It is convenient in the consideration of photolytic processes to regard them, in general, as falling into three groups, which differ somewhat in their causes, namely:

(a) Absorption followed by rupture within one vibration period:

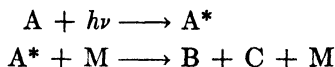


(b) Predissociation; i.e., absorption yielding an activated molecule which sometime thereafter dissociates spontaneously:



where A^* is an activated molecule.

(c) Induced predissociation; i.e., absorption yielding an activated molecule which thereafter decomposes under the influence of an external field; e.g., a magnetic field (see §4.31) or a collision:¹



We have already seen, in the case of the halogens, that the photolysis which occurs may be any of the above types. We have also seen that the particles B and C may be either normal or excited atoms. We shall see, in the case of the polyatomic molecules, that the particles B and C may also be radicals or stable molecules. In some cases photolysis

¹ There is another type of decomposition (like $A^* + A \longrightarrow B + C$) which may be likened to induced predissociation. For a postulated example, see the case of hydrogen iodide, § 7.81.

may produce both types of decomposition. Frequently the phenomena involved are difficult to interpret. However, they repay the efforts of the investigator. When well understood, they offer an insight into the structure of the molecule, the magnitude of the valence forces, the mechanism of decomposition, and the energy of activation.

Oxides

7.2 Ozone. The infrared absorption of ozone is without photochemical significance. The absorption spectra, both in the visible range and in the ultraviolet have been carefully measured; this absorption causes decomposition into molecular oxygen.

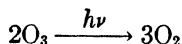


Fig. 23 shows the extinction coefficient of the ozone absorption in the visible range.² The extinction coefficient in the ultraviolet³ is given in Fig. 24 (p. 144). Precise measurements

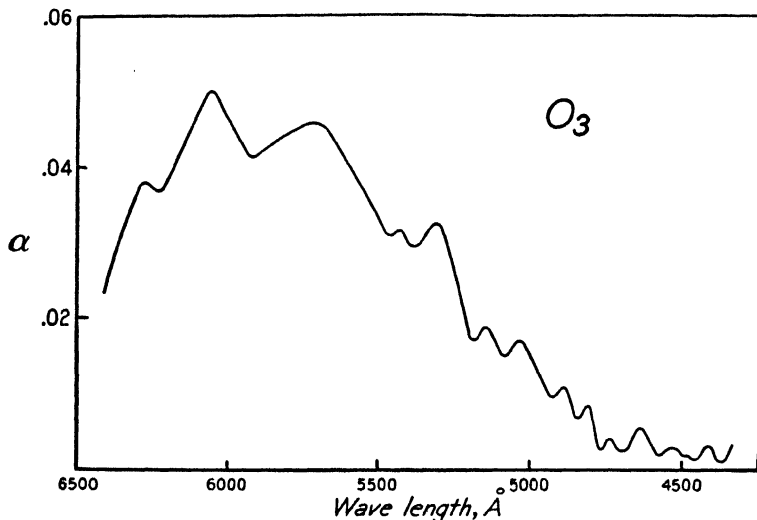


Fig. 23. Extinction Coefficient for Ozone in the Visible Range, according to Colange, *J. phys. rad.*, **8**, 256 (1927). Here α is defined by $I = I_0 \times 10^{-\alpha l}$ at room temperature and atmospheric pressure, where l is expressed in cm.

² Colange, *J. phys. rad.*, **8**, 256 (1927).

³ Lauchle, *Helv. Phys. Acta.*, **1**, 208 (1928); *Z. Physik*, **53**, 92 (1929).

have also been made in the intermediate range 3050–3690 Å.^{4,5} It may be seen from photographs⁶ that the visible

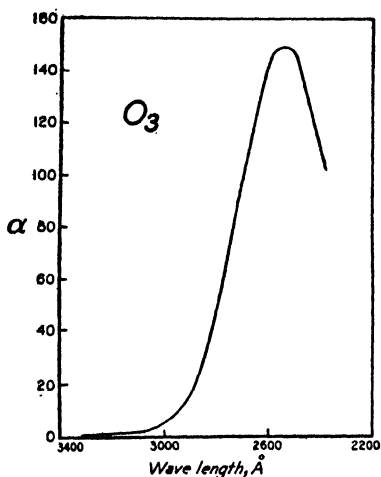
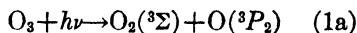


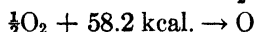
Fig. 24. Extinction Coefficient for Ozone in the Ultraviolet, according to Laüchle, *Helv. Phys. Acta*, **1**, 208 (1928); *Z. Physik*, **53**, 92 (1929). Here α is defined in the same way as for Fig. 23, p. 143.

absorption begins at about 8000 Å.

It is interesting to compare this last figure with calculations on the basis of purely thermochemical data. Obviously the least energy requirement is associated with decomposition of ozone into the ground states; i.e.,



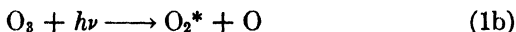
From thermal data,



Therefore



The latter amount of energy corresponds to $\sim 11,800$ Å, which is thus the infrared limit for a possible dissociation. For dissociation in the ultraviolet, according to Heidt,⁷ reaction (1a) is replaced by reaction (1b):



where O_2^* is an excited oxygen molecule. This statement is supported by conclusions of Wulf and Melvin,⁸ according to whom, the spectrum consists of a continuum underlying a band absorption. It appears (see Fig. 25, p. 145) that two band systems are superposed.

Since an arrangement of the band heads into a system has been only partially successful, the extrapolation of the

⁴ Dutheil, *J. Physique Rad.*, **7**, 415 (1926).

⁵ Yakovleva and Kondratjew, *Physik. Z. Sowjetunion*, **9**, 106 (1936).

⁶ Wulf, *Proc. Nat. Acad.*, **16**, 508 (1930).

⁷ Heidt, *J. Am. Chem. Soc.*, **57**, 1710 (1935).

⁸ Wulf and Melvin, *Phys. Rev.*, **38**, 333 (1931).

convergence point to $2700 \text{ \AA}^9$ is quite uncertain. Assuming such a convergence point, it is seen that $\sim 105 \text{ kcal.}$ are

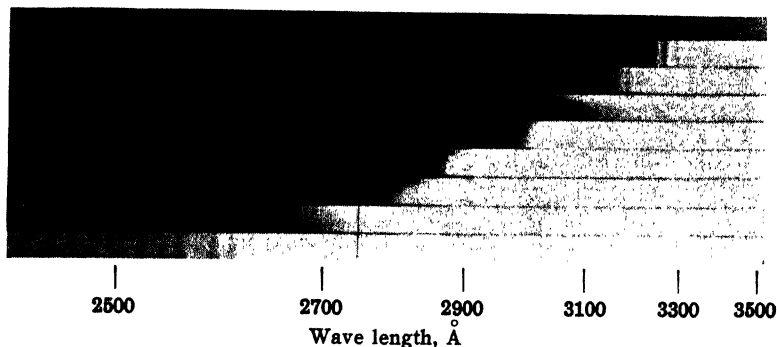
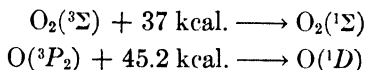
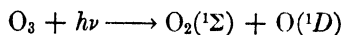


Fig. 25. Photographs of the Absorption Spectrum of Ozone in the Ultraviolet, according to Wulf and Melvin, *Phys. Rev.*, **38**, 333 (1931). The upper photograph is for the maximum length of 2 m. of 4 per cent ozone at 1 atmos.

involved. The amounts of energy involved in the excitation of O_2 and O are



It follows from reaction (1b) that the decomposition into two excited particles involves $24.1 + 37.0 + 45.2 = 106.3 \text{ kcal.}$



Of course, the decomposition into two excited particles occurs only in the ultraviolet continuum (i.e., beyond $\sim 2700 \text{ \AA}$). It may be seen from Fig. 25 that the band spectrum above $2700 \text{ \AA}$ is fuzzy, indicating a possible predissociation. In that range, decomposition produces either an excited oxygen molecule or an excited atom, depending on the conditions, but not both at the same time. Quantum yields for the photolysis of ozone have been determined by Kistiakowsky¹⁰ in the red at $\sim 6200 \text{ \AA}$, and by Warburg¹¹

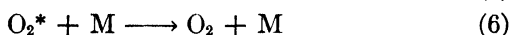
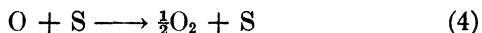
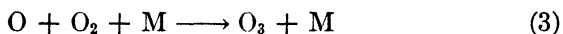
⁹ Kondratjew, *Z. physik. Chem.*, **37**, 70 (1930); Yakovleva and Kondratjew, *Physik. Z. Sowjetunion*, **1**, 472 (1932).

¹⁰ Kistiakowsky, *Z. physik. Chem.*, **117**, 337 (1925); cf. Schumacher, *J. Am. Chem. Soc.*, **52**, 2377 (1930).

¹¹ Warburg, *Sitzb. kgl. preuss. Akad.*, 644 (1913).

and by Heidt and Forbes¹² in monochromatic light in the ultraviolet. Referred to ozone molecules decomposed per quantum absorbed, quantum yields of approximately 2, varying with the initial partial pressures of ozone and oxygen as well as of various inert gases, have been obtained in the red. Heidt^{12b} reports a value of the quantum yield > 4 at wave lengths of 2080, 2540, 2800, and 3130 Å in the ultraviolet.

The results have been subject to searching investigation and analysis by Schumacher and Beretta¹³ and by Heidt^{12b} as well as by Ritchie.¹⁴ According to Heidt, the results are quantitatively explained by the mechanism (subsequent to reaction 1a or 1b):



where M is any energy acceptor including the surface S. According to this mechanism, the atom of oxygen formed in step (1) may, at the maximum, cause further decomposition of one molecule of ozone by step (2). The activated oxygen molecules formed in steps (1b) and (2) propagate the chains. Evidently all the other steps serve to decrease the chain length either by the removal of atomic oxygen in a three-body or wall reaction or by the removal of the chain carrier, the excited oxygen molecule. The reactions involving O_2^* as an energy carrier may be contrasted with the postulated mechanism involving HI^* as a carrier in the photolysis of HI (§ 7.81; cf. § 7.1).

Before the studies of the photochemical decomposition of ozone can be considered completely satisfactory, it seems essential that a study be made of the quantum yields both

¹² (a) Heidt and Forbes, *J. Am. Chem. Soc.*, **56**, 2365 (1934); (b) Heidt, *ibid.*, **57**, 1710 (1935).

¹³ Schumacher, *J. Am. Chem. Soc.*, **52**, 2377 (1930); *Z. physik. Chem.*, **B17**, 405 (1932); Beretta and Schumacher, *ibid.*, **B17**, 417 (1932).

¹⁴ Ritchie, *Proc. Roy. Soc. (London)*, **A146**, 848 (1934).

at a peak and at an adjoining trough in the intermediate region between the continua (i.e., at $\sim 4500\text{--}5000\text{ \AA}$). In this way it may be possible to distinguish the effects due to the bands proper (i.e., predissociation) and to the underlying continua. Further, more complete knowledge of the absorption spectrum itself might require substantial revision of the suggested mechanisms. No work has been done on pure ozone at low pressures. It is possible (cf. the case of sulfur, § 4.4) that sharpening of the bands may occur at such pressures, a result showing that we are actually concerned with induced predissociation (§ 4.31) rather than simple predissociation in the band region. In this connection it is particularly noteworthy that O_2 , which is the usual contaminant, and O_3 are both paramagnetic and consequently excellent inducers of forbidden transitions.

7.3 Other oxides of the oxygen family. According to this classification, ozone (just discussed) is the first oxide of the oxygen family. Of the sulfur oxides, only SO_2 and SO_3 have been subjected to photochemical study. They are described in detail below. The absorption spectra of TeO_3 and MoO_3 have been photographed and discussed by Dutta and Sen-Gupta.¹⁵

7.31 Sulfur dioxide. Sulfur dioxide has been the most completely studied of the oxides of sulfur. Its absorption spectrum has been investigated extensively in the near ultraviolet by Watson and Parker,^{16a} and in the vacuum ultraviolet by Price and Simpson,^{16b} as well as by others.¹⁷ Lotmar¹⁸ was able to excite a fluorescence spectrum in sulfur dioxide by absorption of the Zn line $2100\text{ \AA}$. According to Henri,^{17a} the ultraviolet absorption spectrum of SO_2 may be divided into three regions:

(1) A region extending from 3950 to $3400\text{ \AA}$. It is ex-

¹⁵ Dutta and Sen-Gupta, *Proc. Roy. Soc. (London)*, **A139**, 397 (1933).

¹⁶ (a) Watson and Parker, *Phys. Rev.*, **37**, 1013 (1931); (b) Price and Simpson, *Proc. Roy. Soc. (London)*, **165**, 272 (1938).

¹⁷ (a) Henri, *The Structure of Molecules*, P. Debye, Editor, Blackie and Son, London, 1932, p. 134; (b) Asundi and Samuel, *Proc. Indian Acad. Sci.*, **2A**, 30 (1935).

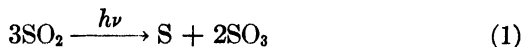
¹⁸ Lotmar, *Z. Physik*, **83**, 765 (1933).

hibited at high pressure (≥ 1 atm. for thickness of layer, $d = 100$ cm.) and consists of a number of very fine bands with sharp rotation lines.

(2) A banded region extending from 3480 to ~ 2400 Å. It appears even at a pressure of 0.1 mm. (for $d = 100$ cm.) and attains its limiting extension at 700 mm. pressure. It shows a maximum at 2850 Å. Above 2850 Å, the bands of this region are very sharp and exhibit a good rotation spectrum, especially when photographed at -80° . At 2800 Å, the bands become blurred and broaden out as they approach the ultraviolet. Beyond 2550 Å, only completely diffuse absorption bands appear.

(3) A region extending from 2445 Å far into the ultraviolet. This region appears at pressures of 0.02 to 10 mm. Sharp bands with quantized rotation are obtained down to 1950 Å, after which the bands become rapidly more diffuse. According to Price and Simpson,^{16b} the principal characteristic of the bands below 1950 Å is their increase in multiplicity and departure from regularity.

There is by no means good agreement as to the interpretation to be put on these observations. At low temperatures the principal reaction appears to be

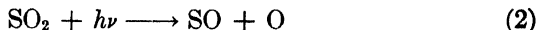


The heat of dissociation of SO_2 into $\text{S} + 2\text{O}$ is ~ 253 kcal. If we adopt the value of Martin and Jenkins¹⁹ for the heat of dissociation of SO (i.e., 117.6 kcal.), it appears that dissociation of SO_2 into $\text{SO} + \text{O}$ requires only ~ 135 kcal., corresponding to 2105 Å. The diffuseness of the bands at the higher wave lengths could then be ascribed only to pressure broadening. The appearance of fluorescence at 2100 Å is good evidence that dissociation does not occur at that wave length. Apparently predissociation sets in at ~ 1950 Å, corresponding to ~ 145 kcal. The excess energy of ~ 10 kcal. ($145 - 135 = 10$ kcal.) is insufficient to excite the oxygen atom²⁰ and, as pointed out by Franck, Sponer,

¹⁹ Martin and Jenkins, *Phys. Rev.*, **39**, 549 (1932).

²⁰ Note the reaction $\text{O}(^3P_2) + 45.4 \text{ kcal.} \rightarrow \text{O}^*(^1D_2)$.

and Teller,²¹ is distributed as energy of vibration and translation in the products of the primary reaction



The photochemical evidence as to the nature of the primary step is largely indirect. In some of the work the problem has been approached through a study of the associated reaction of SO_2 with oxygen to give SO_3 .²² The absence of a reaction at $\lambda = 2537 \text{ \AA}$ has been ascribed to failure of the SO_2 to dissociate. The reaction which occurs at shorter wave lengths may be due to activation of the oxygen, which also absorbs those wave lengths. The blurring of the spectrum at $\lambda < 1950 \text{ \AA}$ indicates that dissociation occurs at such wave lengths.

Wieland²³ showed that, on illumination at 450° , the bands due to SO_2 almost completely vanish and are replaced by a new spectrum due to S_2 , consisting of very faint bands between 2800 and 2600 $\text{\AA}$ and of a much stronger band system below 1800 $\text{\AA}$. After the absorption tube is recooled, the SO_2 bands reappear with the same intensity as before heating. When SO_2 is irradiated with light of $\lambda \simeq 1860 \text{ \AA}$ at -78° to -70°C. , the absorption spectrum between 3100 and 2500 $\text{\AA}$ before, during, and after irradiation is substantially unaltered.²⁴ Although small traces of sulfur are found after irradiation, the absorption bands of SO are invisible, even though they should be readily detected if present. This observation cannot be the result of a subsequent decomposition of SO , for Cordes and Schenk²⁵ have presented good evidence as to the stability of the latter.

It might seem that reaction (2) is not a good picture of the primary step, since Cordes and Schenk have shown that the SO molecule is extremely non-reactive toward SO_2 , O_2 , or SO in the gas phase. However, it has been shown above that the SO produced in reaction (2) probably has

²¹ Franck, Sponer, and Teller, *Z. physik. Chem.*, **B18**, 88 (1932).

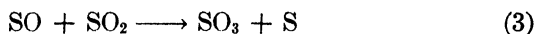
²² Kornfeld and Weegman, *Z. Elektrochem.*, **36**, 789 (1930).

²³ Wieland, *Trans. Faraday Soc.*, **30**, 260 (1934).

²⁴ Kornfeld and McCaig, *ibid.*, **30**, 991 (1934).

²⁵ Cordes and Schenk, *Z. anorg. allgem. Chem.*, **214**, 33 (1933).

some excess energy, perhaps of vibration. Kornfeld and McCaig suggest that this excess energy could be considered responsible for a high probability of reaction of SO with O₂ or another SO, and that the latter reaction would have to compete with



at higher temperatures. The atomic sulfur so formed would enter into the reaction



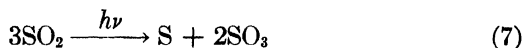
thus initiating chains. The failure to detect SO under the conditions of the thermo-optical dissociation discovered by Wieland is traced to the alternative mechanisms (3)–(4) or (5)



where it is assumed that activated SO molecules possess a reactivity not characteristic of the normal molecules. The O atom produced in step (1) obviously disappears by the reaction



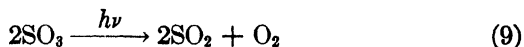
From reactions (5) and (6) it may be seen that the limiting overall reaction at low temperatures is



Konstantinova-Schlezinger²⁶ states that the yield is cut down by the (dark) back reaction



as well as by the photoreaction

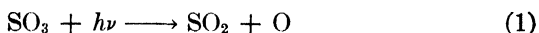


It should be mentioned that, at the higher temperatures used by Wieland, there is another source of increased yield beyond that suggested by Kornfeld and McCaig. According to Franck, Spöner, and Teller, the photoactive range is

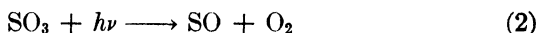
²⁶ Konstantinova-Schlezinger, *J. Phys. Chem.* (U.S.S.R.), **6**, 601 (1935).

increased by the rise in temperature, the predissociation limit probably being shifted toward the visible. Of course, the measured quantum yield is not thereby necessarily increased. However, the effective range of the arc is altered.

7.32 Sulfur trioxide. Taking particular precautions to exclude the effects of SO_2 , Fajans and Goodeve²⁷ observed the absorption spectrum of SO_3 between 3000 and 2200 Å. The continuum seems to begin at ~ 3100 Å. The absorption spectrum consists of weak diffuse bands superimposed on a continuous background. The observed diffuse bands are of an unusual type; the maxima of absorption are flat, and the minima sharp. Kornfeld²⁸ has shown that SO_3 is decomposed by light of 2750 Å and has interpreted the results as indicating that the primary step is the reaction



which requires 82.1 kcal. and is therefore energetically possible below 3460 Å. The reaction



requires 103.4 kcal. and is therefore energetically possible at 2750 Å. However, since there is no extraordinary increase in the rate of photolysis on extending the light range to 2650 Å, Kornfeld concludes that reaction (2) is unlikely. The decomposition yielding an excited (^1D) O atom requires an additional 45 kcal. and is therefore energetically possible only below ~ 2230 Å.

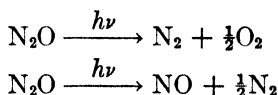
7.4 Oxides of nitrogen. Of the four oxides of nitrogen which have been subjected to photochemical investigation, all are decomposed by the light which they absorb. Nitrogen pentoxide is also decomposed in a sensitized reaction involving nitrogen dioxide ($\text{NO}_2\text{-N}_2\text{O}_4$), and will consequently be further discussed in the chapter on photosensitization. The literature makes no mention of any photochemical study of nitrogen trioxide (nitrous anhydride).

²⁷ E. Fajans and C. F. Goodeve, *Trans. Faraday Soc.*, **32**, 511 (1936).

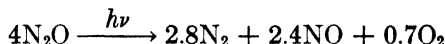
²⁸ Kornfeld, *Trans. Faraday Soc.*, **33**, 614 (1937).

7.41 Nitrous oxide. The absorption spectrum of nitrous oxide has been studied frequently.²⁹ There are two regions of continuous absorption: one, at 2200 to 1700 Å; the other, beginning at 1580 Å and extending far into the ultraviolet.

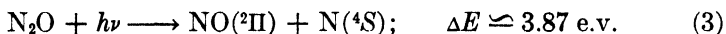
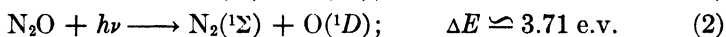
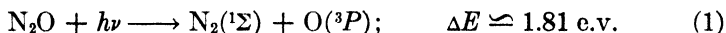
The photodecomposition in the Al spark region 1990 to 1860 Å has been investigated both by Macdonald³⁰ and by Noyes.³¹ The results obtained by Noyes can be represented by two unequal overall reactions



the net result of which approximates to

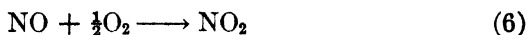
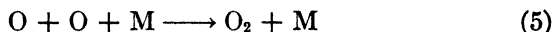


This is slightly different from the overall equation originally given by Macdonald. From his results, Macdonald concluded that the initial step is an excitation of a nitrous oxide molecule followed by collision and reaction with an unexcited molecule. However, the more recent work of Noyes has shown that, of the three possible initial steps,



the primary decomposition is almost certainly according to reaction (1) or (2).

Any of the three steps is energetically possible below 3190 Å. However, the results of Noyes on the photolysis of pure N₂O and of N₂O in the presence of mercury vapor are best explained by reaction (1) or (2) followed by

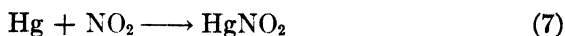


²⁹ Cf. (a) Henry, *Compt. rend.*, **200**, 656 (1935); *J. chim. phys.*, **32**, 437 (1935). (b) Sen-Gupta, *Nature*, **136**, 513 (1935); *Bull. Acad. Sci. United Provinces Agra Oudh* (India), **3**, 197 (1934). (c) Duncan, *J. Chem. Phys.*, **4**, 638 (1936).

³⁰ Macdonald, *J. Chem. Soc.*, 1 (1928).

³¹ W. A. Noyes, Jr., *J. Chem. Phys.*, **5**, 807 (1937).

Of the gaseous content of the mixture, NO, O₂, and N₂ are all volatile at the temperature of boiling liquid air. Per quantum absorbed, the yield of molecules uncondensed by liquid air, γ_2 , is 1.3 ± 0.2 . If mercury is present, the nitrogen dioxide reacts with it slowly, according to the steps



Consequently, per quantum absorbed, the yield of uncondensed products in the presence of mercury vapor, γ_1 , may be expected to be higher; actually, $\gamma_1 = 1.9$.

Noyes has shown that the results are compatible with the mechanism suggested; for, if we let

$$n_1 = \text{N}_2\text{O disappeared}$$

$$n_2 = \text{N}_2 \text{ formed}$$

$$n_3 = \text{NO formed}$$

$$n_4 = \text{O}_2 \text{ formed}$$

then, obviously,

$$n_1 = n_2 + \frac{1}{2}n_3 = 2n_4 + n_3$$

when a sufficient excess of NO is formed to consume all the O₂ according to reaction (6). Since $n_2 = 1$ and it is an experimental fact that $\gamma_1 = 1.9$, in the presence of mercury

$$\gamma_1 = n_2 + n_3$$

$$1.9 = 1 + n_3$$

Therefore, $n_3 = 0.9$, and $2n_4 + 0.9 = 1 + 0.45$ or $n_4 = 0.275$. In the absence of mercury, it is clear that

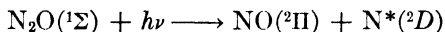
$$\begin{aligned} \gamma_2 &= n_2 + n_3 + n_4 + 3n_4 \\ &= 1 + 0.45 + 0.275 + 0.825 \\ &= 1.35 \end{aligned}$$

a result which is evidently in close agreement with the average experimental value $\gamma_2 = 1.3 \pm 0.2$.

It has been pointed out by Noyes that the weakness of the absorption suggests the transition is forbidden, and that it is possible the N₂ molecules and the O atoms are produced

in their normal electronic states with perhaps some vibrational energy in the nitrogen molecule. Although at least part of the primary split must be into N_2 molecules and O atoms, Noyes states that the possibility of reaction (3) has not been definitely excluded.

On the other hand, it should be mentioned that evidence cited by Henry^{29a} in favor of reaction (3) is by no means satisfactory. For example, the detection of the NO bands at 2261 and 2268 Å is without significance, since the presence of NO is adequately explained by the mechanism suggested by Noyes. As for evidence on the basis of energetics alone, it is well to recall that, although any mechanism suggested must be energetically possible, energetic possibility alone is no indication of the actuality of a particular mechanism. Henry has shown that the wave length of the beginning of the continuum increases with temperature, being 2246 Å at 20° and 2604 Å at 275°. By extrapolating to 0°K., he finds that the beginning of the continuum then corresponds to 132 kcal. and concludes, solely on the basis of energetics and what may be entirely fortuitous "approximate" agreement of calculation with experiment,³² that the initial reaction is



Such evidence, of course, is inconclusive. The mechanism suggested by Noyes, based on chemical as well as energetic grounds, is consequently more acceptable.

7.42 Nitric oxide. The absorption spectrum of nitric oxide has been studied by Leifson³³ and by Lambrey.³⁴ Flory and Johnston³⁵ have analyzed the bands, according to the data of Leifson and of Lambrey, with the result shown in Fig. 26 (p. 155). There is no evidence of the beginning of a continuum down to the limit of observation at ~ 1300 Å. The photolysis at pressures of 70 to 630 mm. was studied

³² For the calculations, see the original papers, ref. 29a.

³³ Leifson, *Astrophys. J.*, **63**, 73 (1926).

³⁴ Lambrey, *Compt. rend.*, **189**, 574 (1929); **190**, 670 (1930); *Ann. phys.*, **14**, 95 (1930).

³⁵ Flory and Johnston, *J. Am. Chem. Soc.*, **57**, 2641 (1935).

by Macdonald³⁰ in a wave length range of 1990–1860 Å; Flory and Johnston³⁵ studied the photolysis at pressures of

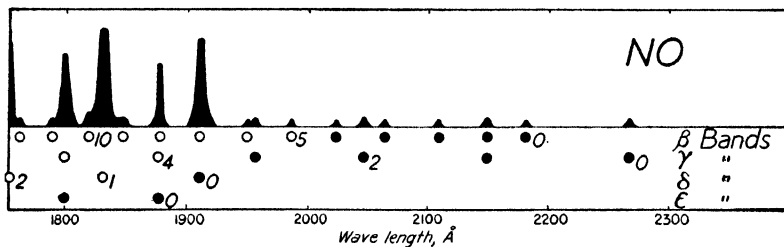
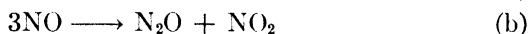


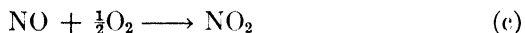
Fig. 26. Absorption Spectrum of NO, as analyzed by Flory and Johnston, *J. Am. Chem. Soc.*, **57**, 2641 (1935), from the data of Leifson and of Lambrey. The heights of the peaks are measures of the relative intensities. Open circles mark bands absent in emission.

0.02 to 7.12 mm. over a greater range of wave length, i.e., 2537–1775 Å.

According to Macdonald, nitric oxide can decompose by one of two overall reactions



with about 90 per cent of the decomposition taking place according to reaction (a). At the high pressures used by Macdonald, the oxygen formed disappears by the reaction

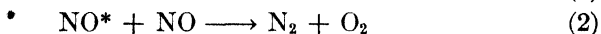


Assuming an average wave length of 1900 Å, Macdonald determined that 1.45 molecules of NO disappeared per quantum absorbed. Making allowance for the NO disappearance in reaction (c), he calculated that the quantum yield of NO decomposed was 0.75.

Flory and Johnston established that at low pressures the effective radiation is 1832 Å; i.e., the reaction is due to absorption in the δ (1,0) band. They showed that absorption of λ 1849 Å in the β (9,0) band may have a smaller effect, which becomes significant at higher pressures; i.e., above 33 mm. and in the pressure range studied by Macdonald. The dissociation energy of N_2 seems to be definitely fixed in

the neighborhood of 7.34 e.v.³⁶ Combining this value (equivalent to 169.3 kcal. per mole) with that of the heat of dissociation of oxygen (117.3 kcal.)³⁷ and with the heat of formation of nitric oxide at absolute zero,³⁸ they obtain a value of ~ 122 kcal. as the energy required for the decomposition of NO into atoms at 0°K. It thus appears that the decomposition is *energetically* possible at all wave lengths below ~ 2320 Å. However, as has already been repeatedly indicated, this does not insure that reaction actually takes place at such wave lengths.

Perhaps primarily because the active radiation falls in a banded region of the spectrum, Macdonald originally attributed the simple dissociation process to the successive reactions



However, Flory and Johnston studied not only the effect of varying pressure of nitric oxide but also that of an added inert gas (namely, nitrogen). They concluded that the nature of the dependence of reaction rate on nitric oxide pressure (it was shown that the rate was determined solely by the amount of light absorbed) and its independence of nitrogen pressure indicated that the primary step is a spontaneous dissociation



and, since the dissociation process occurs in the banded region, a predissociation is involved.

The relationships involved are shown in the potential energy diagram of Fig. 27, which, except for the $^4\Pi$ state, is as shown by Flory and Johnston. At low pressures, as already stated, the effective absorption is the δ (1,0) band. Predissociation takes place to the $^2\Sigma$ repulsive level, whose position is estimated from the following considerations:

³⁶ Herzberg and Sponer, *Z. physik. Chem.*, **B26**, 1 (1934); Mulliken, *Phys. Rev.*, **46**, 144 (1934).

³⁷ Herzberg, *Z. physik. Chem.*, **B10**, 189 (1930). See, however, Appendix II, Table 30.

³⁸ Giaque and Clayton, *J. Am. Chem. Soc.*, **55**, 4875 (1933).

(1) Kaplan³⁹ attributes the absence of β emission bands with v' greater than 4 (and the unexpected weakness of $v' = 4$ bands) to predissociation to a repulsive level which must intersect the upper ${}^2\Pi$ curve somewhere in the neighborhood of $v' = 4$.

(2) A similar explanation may be offered for the absence of δ emission bands⁴⁰ with $v' > 0$, although strong emission bands would be expected for higher vibration states, on the basis both of the Franck-Condon principle and of the distribution in absorption.

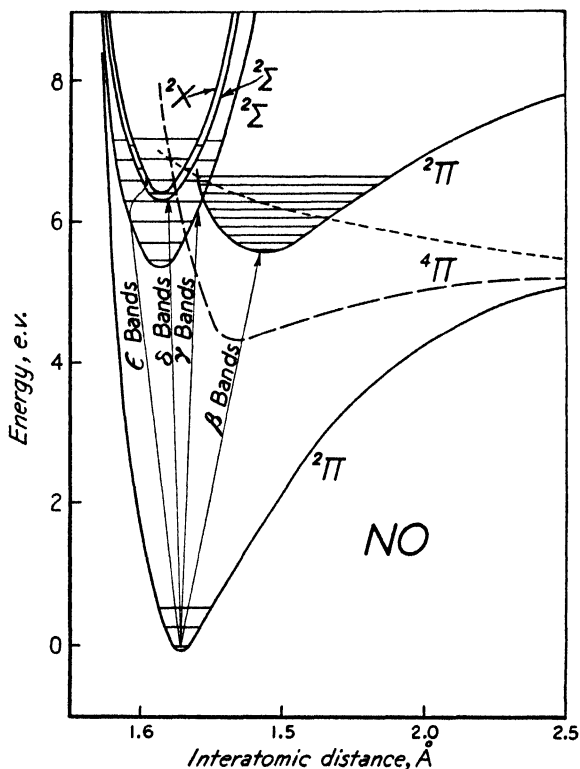


Fig. 27. Potential Energy Curves for the Known States of NO. The dotted repulsive curve represents the estimated position of the ${}^2\Sigma$ state responsible for predissociation in the region $\lambda = 2000\text{--}1800 \text{ \AA}$.

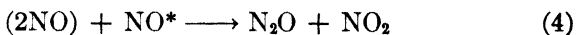
³⁹ Kaplan, *Phys. Rev.*, **37**, 1406 (1931).

⁴⁰ Knauss, *Phys. Rev.*, **32**, 417 (1928). Schmid, *Z. Physik*, **59**, 42, 850 (1929); **64**, 279 (1930).

(3) Absorption of λ 1849 Å in the β (9,0) band effects decomposition at higher pressures.

Flory and Johnston state their expectation that any of the bands marked by open circles in Fig. 26 would be photochemically active, while radiation absorbed by bands marked with black circles would be inactive, except for some activity in the β (4,0) band. In the light of Fig. 27, this statement requires no further explanation. However, Wulf⁴¹ has called attention to one other interesting point. Lambrey has shown that there is a remarkably strong broadening of the γ bands at high pressures. Wulf attributes this phenomenon to a weakening of the selection rules by collision so as to make possible (induced) predissociation from the $^2\Sigma$ level of the γ bands into the low-lying $^4\Pi$ level, which dissociates into normal atoms. Both multiplicity and angular momentum change in this case and are normally forbidden. This is an excellent example of collision weakening the selection rules (cf. §§ 4.31, 7.1). On the other hand, as might be expected, Lambrey detected no such broadening of the β bands. It is interesting to note that the position of the $^4\Pi$ potential curve was qualitatively predicted by Mulliken⁴² prior to Wulf's explanation of the γ broadening. Although its position is such as to permit induced predissociation from the $^2\Sigma$ curve, it does not intersect or approach the $^2\Pi$ curve which is the upper state of the β bands. Consequently, the latter do not broaden at high pressures as do the γ bands.

On the basis of their own work and a consideration of the energy relationships involved, Flory and Johnston are inclined to discount Macdonald's statement that N_2O is among the products of the dissociation of nitric oxide. In order to account for such a reaction, Macdonald cited the existence of a double NO complex⁴³ and postulated a reaction of the type



⁴¹ Wulf, *Phys. Rev.*, **46**, 316 (1934).

⁴² Mulliken, *Rev. Mod. Phys.*, **4**, 1 (1932).

⁴³ Cf. O. K. Rice, *J. Chem. Phys.*, **4**, 367 (1936).

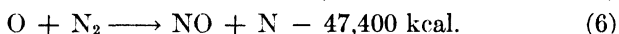
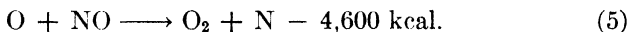
However, in view of Flory and Johnston's picture of the photolysis, it is doubtful whether an activated NO molecule has sufficient persistence for such a reaction, except at high pressures.

We may now return to a consideration of the various steps following on the primary split of reaction (3). The latter takes place principally at 1830 Å; i.e., with an energy input ~ 33.6 kcal. in excess of the minimum required (122 kcal.). Both momentum and energy must be conserved in the dissociation. Consequently we may write two simultaneous equations

$$\begin{aligned} m_N v_N + m_O v_O &= 0 \\ \frac{1}{2} m_N v_N^2 + \frac{1}{2} m_O v_O^2 &= 33.6 \text{ kcal.} \end{aligned}$$

where m and v are atomic weights and velocities of the N and O atoms respectively. Solving these equations, we find that the kinetic energies given to the nitrogen and oxygen per gram atom are ~ 15.7 and 17.9 kcal. per gram atom.

Of the various stoichiometrically possible secondary reactions, Flory and Johnston reject the following on energetic grounds:



Reaction (6) is obviously improbable. As for reactions (5) and (7), they point out that in collision of a fast oxygen atom with either nitrogen or nitric oxide in the gas phase, conservation of linear momentum exacts a minimum toll of 35 per cent of the kinetic energy of the oxygen. This leaves only ~ 10 kcal., as a maximum for activation. In only a small fraction of the collisions is this maximum energy available. The great majority of collisions are elastic, because of steric and statistical factors, and dissipate the high energy of the oxygen in successive small losses. As for reaction (7), it may be pointed out that, as a matter of fact, added nitrogen had no effect on the rate of the

photolysis. After considering other possible secondary reactions, Flory and Johnston conclude that it appears reasonable to credit the entire secondary process, in the main, to the simple set of wall reactions:



Reaction (9), of course, accounts for Macdonald's observation that the quantum yield of the decomposition is less than 1.0.

Experimental work still remains to be done with NO at higher pressures, particularly to establish the nature of the predissociation in β and γ bands. Furthermore, it would be well to know whether N_2O is actually formed and, if so, during which absorption processes.

7.43 Nitrogen dioxide. The absorption spectrum of nitrogen dioxide is the combined spectrum of NO_2 and N_2O_4 . The equilibrium $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ is established practically instantaneously; the partial pressure of either constituent in a mixture can be determined from the data of Verhoek and Daniels.⁴⁴ The mixture absorbs over the full range from the visible to the short ultraviolet. The absorption has been studied frequently.⁴⁵

The spectrum of NO_2 is, as shall be apparent later, our primary concern. The reddish brown color of the mixture

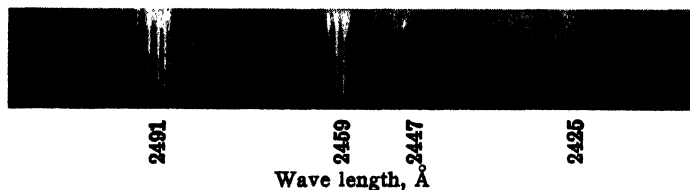
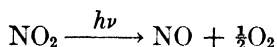


Fig. 28. Predissociation Spectrum of NO_2 , according to Henri, *Trans. Faraday Soc.*, **25**, 765 (1929).

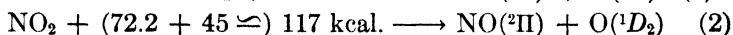
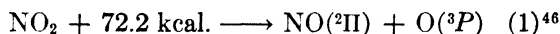
⁴⁴ Verhoek and Daniels, *J. Am. Chem. Soc.*, **53**, 1250 (1931).

⁴⁵ Cf. (a) Leifson, *Astrophys. J.*, **63**, 73 (1926); (b) Harris, *Proc. Nat. Acad.*, **14**, 690 (1928); (c) Carwile, *Astrophys. J.*, **67**, 184 (1928); (d) Henri, *Nature*, **125**, 202 (1930); (e) Mecke, *Naturwissenschaften*, **17**, 996 (1929); (f) Lambrey and Corbiere, *Compt. rend.*, **201**, 1334 (1935).

is due to the presence of this constituent. The spectrum begins with a region of closely packed lines and line groups at about 6000 Å. Blurring begins at about 3700 Å, where the bands become broad and diffuse, presumably on account of the inception of predissociation. The blurring continues until 2596 Å, where the weak diffuse bands are suddenly replaced by sharply defined bands, attributed by Henri ^{46a} to another electron jump. Then, suddenly, at 2459 Å blurring recommences. The overall reaction for the photolysis of nitrogen dioxide is



Two types of dissociation are energetically possible for the primary step



Reaction (1) yields both nitric oxide and oxygen in the normal state, whereas reaction (2) produces an excited O atom. The difference in the energy requirement of the two reactions is obviously the amount of energy required to excite the O atom. Since 72.2 kcal. corresponds to ~ 3900 Å, it is therefore reaction (1) that occurs at 3700 Å. Similarly, 117 kcal. corresponds to 2430 Å, and reaction (2) first occurs at 2459 Å. The slight energy deficiency is perhaps traceable to errors in the calculation.

The relationships are illustrated qualitatively in the potential energy diagram of Fig. 29 (p. 162).⁴⁷ Electron jumps can occur from the normal NO₂ curve to either of the two excited states. Predissociation from curve *a* to curve *a'* is obviously possible at all energy levels near their intersection; whereas, for curve *b*, predissociation to curve *b'* can occur only at levels at or above the intersection, thus qualitatively accounting for the sharpness of the 2459 Å

⁴⁶ Mecke, *Z. physik. Chem.*, **B7**, 127 (1930); Herzberg, *ibid.*, **B10**, 189 (1930). Cf. Franck, Sponer, and Teller, *ibid.*, **B18**, 88 (1932).

⁴⁷ Fig. 29 is slightly different (i.e., in the position of the *b'* curve) from that given by Herzberg, *Ergeb. exakt. Naturw.*, Julius Springer, Berlin, 1931, **10**, 257.

predissociation limit. It may be seen that the close correspondence between the observed and "energetically possible" wave length limits of reaction (2) is accounted for by the arrangement of potential curves shown.

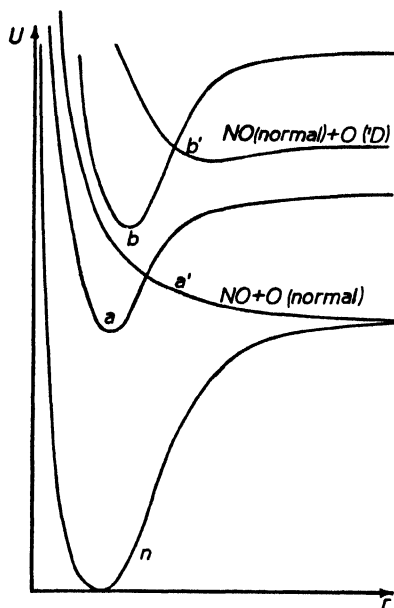


Fig. 29. Potential Energy Curves for NO_2 .

The ultraviolet absorption curve for N_2O_4 in the range 4105–3200 Å has been found to be slightly different from that of NO_2 .^{45f}

The quantum yield of the photolysis has been studied by Dickinson and Baxter,⁴⁸ by Norrish,⁴⁹ and by Holmes and Daniels.⁵⁰ Proper correction has been made for the (dark) back reaction $\text{NO} + \frac{1}{2}\text{O}_2 \rightarrow \text{NO}_2$. All agree that some decomposition occurs at 4050 Å and none at 4360 Å. The results of Holmes and Daniels, who succeeded in divorcing the separate phenomena involved in

the photolyses of NO_2 and N_2O_4 by a wide range of studies involving the use of N_2O_6 , are quoted below. Evidently, the limiting quantum yield for the NO_2 decomposition is 2.0 at the shorter wave lengths.

According to Table 11 (p. 163), dissociation sets in before the "energetically possible" value of ~ 3900 Å. The slight energy deficiency may be supplied by the vibrational energy present in the NO_2 molecule at ordinary temperatures. The sharpness of the bands at 4050 Å is an indication of the long life of the activated state. The dissociation occurs

⁴⁸ Dickinson and Baxter, *J. Am. Chem. Soc.*, **50**, 774 (1928).

⁴⁹ Norrish, *J. Chem. Soc.*, 1158, 1604, 1611 (1931).

⁵⁰ Holmes and Daniels, *J. Am. Chem. Soc.*, **56**, 630 (1934).

more readily as the amount of energy absorbed is increased. The angle at which the a and a' curves cross in Fig. 29 is a good pictorial representation of why predissociation does not always occur. It has already been stated (§ 4.3) that the conditions for predissociation are best when the angle between the intersecting curves is small. It must be re-

TABLE 11
QUANTUM YIELDS IN THE PHOTOLYSIS OF NO_2 AND N_2O_4

λ , Å	NO_2	N_2O_4
4360	0.0	t
4050	0.50	t
3660	1.83	0
3130	1.93	0
2800	2*	Small
2650	2*	0.4

Note. t indicates transparent; *, assumed.

membered that predissociation is not necessarily accompanied by blurring of the bands. Blurring occurs only when the lifetime of the excited molecule becomes short; the higher the energy content of the excited molecule, the shorter its life. Thus the bands become diffuse only at the shorter wave lengths, but predissociation has already set in. The characteristics of predissociation are discussed in § 4.3. It is important to remember that a two-dimensional potential energy diagram, such as Fig. 29, is an extremely qualitative picture of a tri-atomic system.

It is interesting to note that Norrish studied the fluorescence of nitrogen dioxide in the range 1 to 100 mm. Hg and, in agreement with expectation, found that, although fluorescence occurs on illumination at 4360 Å, it is weak at 4050 Å and practically absent at 3650 Å. Thus it is clear that, at ≤ 4050 Å, an excited molecule may either dissociate or fluoresce. At 3650 Å, dissociation of NO_2 occurs almost exclusively.

As for N_2O_4 , it may be seen from Table 11 that the prediction of Dawsey⁵¹ that it should be decomposed by the light

⁵¹ Dawsey, *Proc. Nat. Acad. Sci.*, **16**, 546 (1930).

which it absorbs is only partially confirmed by the results. The case of nitrogen tetroxide, near the beginning of its predissociation region, may be an illustration of one of the types mentioned by Franck, Sponer, and Teller²¹ (cf. § 4.7) in which blurring of the spectrum of a large molecule occurs without dissociation. There is also the possibility⁵⁰ that at longer wave lengths the N_2O_4 undergoes photolysis into two NO_2 molecules, which immediately recombine thermally and thus prevent pressure change.

7.44 Nitrogen pentoxide. The absorption spectrum of this compound has been studied by Urey, Dawsey, and Rice,⁵² and by Dutta and Sen-Gupta.⁵³ The former report a continuum beginning at $\sim 3050 \text{ \AA}$ and extending into the ultraviolet, whereas the latter state that the continuum begins at $\sim 4500 \text{ \AA}$, extends to $\sim 3200 \text{ \AA}$ where the gas becomes transparent, and resumes at $\sim 2800 \text{ \AA}$. However, in the earlier work, ozone was present as a deliberately added impurity, whereas, in the latter, correction had to be made for the accidental presence of NO_2 . Jones and Wulf⁵⁴ have attempted to avoid these difficulties by following the absorption spectrum of N_2O_5 in the presence of O_3 gradually changing into O_2 . In this way, it was possible to determine the absorption at the time corresponding to the moment of complete disappearance of ozone, before the formation of NO_2 may be presumed to interfere. They concluded that weak continuous absorption is existent at $3800 \text{ \AA}$ and increases rapidly at $2800 \text{ \AA}$, without any trace of a maximum down to $2400 \text{ \AA}$. There is evident disagreement among the three methods. However, there is clear evidence that a continuum exists at $2800 \text{ \AA}$ and extends toward the far ultraviolet.

The only successful photochemical investigation of pure nitrogen pentoxide is by Holmes and Daniels,⁵⁵ who found that it is decomposed into nitrogen dioxide and oxygen

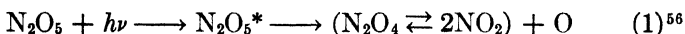
⁵² Urey, Dawsey, and Rice, *J. Am. Chem. Soc.*, **51**, 3190 (1929).

⁵³ Dutta and Sen-Gupta, *Proc. Roy. Soc. (London)*, **A139**, 397 (1933).

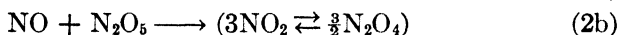
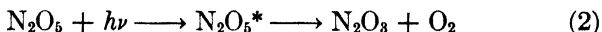
⁵⁴ E. J. Jones and Wulf, *J. Chem. Phys.*, **5**, 873 (1937).

⁵⁵ Holmes and Daniels, *J. Am. Chem. Soc.*, **56**, 630 (1934); cf. Baxter and Dickinson, *ibid.*, **51**, 109 (1929).

by light absorbed at 2800 and 2650 Å with a quantum efficiency of 0.6. Urey, Dawsey, and Rice⁵² pointed out that the energy below 3000 Å is sufficient to effect the reaction



Part of the failure to obtain a quantum yield of unity may be due to reoxidation of the nitrogen peroxide by atomic O or O₃.⁵⁷ On the other hand, if the reaction proceeds according to the mechanism



the efficiency of the photoprocess is only 0.3 and the low efficiency cannot be attributed to the reoxidation of nitrogen dioxide. However, if the absorption is really in a continuum, it seems more probable that mechanism (1), omitting the intermediate state N₂O₅^{*}, is correct and that the low yield is actually caused by a back reaction.

The catalyzed photodecomposition of N₂O₅ is discussed in the chapter on photosensitization (§10.53).

7.45 NO₃. Photographs of the visible absorption spectrum of NO₃ have been published by Jones and Wulf.^{54, 58} Absorption bands were detected at ~ 7100 Å. There are several absorption maxima in the visible, the most prominent occurring at ~ 6650 Å and ~ 6280 Å. The absorption spectrum is complicated, and Jones and Wulf suggest that studies at higher dispersion may show considerable detail. There is no evidence of a continuum.

7.46 Nitrosyl chloride. Absorption by NOCl begins at ~ 6500 Å and increases gradually toward the ultraviolet.^{58a} A region of diffuse banded absorption extends to 4000 Å, beyond which point the spectrum is continuous. Maxima

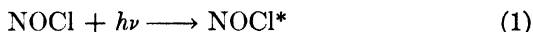
⁵⁶ Jones and Wulf have used the data of Bichowsky and Rossini, *Thermochemistry of Chemical Substances*, Reinhold Publishing Corp., New York, 1936, and have calculated the necessary energy for the reaction $\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + \text{O}(^3P_2)$ to be 61.16 kcal., which corresponds to ~ 4660 Å.

⁵⁷ Cf. §12.3 for the formation of O₃.

⁵⁸ Cf. Sprenger, *Z. Elektrochem.*, **37**, 674 (1931).

^{58a} Kistiakowsky, *J. Am. Chem. Soc.*, **52**, 102 (1930).

are situated at about 5990, 4690, 3300, and < 2500 Å. The region 6500–5500 Å possesses line structure. The quantum yield of the photolysis to NO and Cl₂ was found to be 2.0 in the range 6300–3650 Å. Wave lengths of ≤ 6400 Å (corresponding to > 44.3 kcal.) were found to be effective. A mechanism suggested was



On the basis of the available thermal data,^{58a, b} 37.8 kcal. is required to dissociate the molecule into NO and Cl. Thus the evidence may also be interpreted in favor of the simple predissociation mechanism



It was found that added nitrogen decreased the reaction velocity. The banded nature of the absorption is in accord with either mechanism.

7.5 Halogen oxides. Very little is known about the photodecomposition of these substances. There is no information available on any iodine oxide.

7.51 Oxides of fluorine. F₂O has been studied by Glissman and Schumacher.⁵⁹ Absorption begins at ~ 5400 Å, and is continuous with maxima at 4210, 3580, 2940 Å and some other wave length at less than 2100 Å. On energetic grounds, Glissman and Schumacher attribute the first three maxima to dissociation into F₂ + O or F + FO; the maximum below 2100 Å is, on the other hand, attributed to dissociation into F + F + O. In the actual experiments in glass or quartz vessels, SiF₄ and O₂ are formed. Inasmuch as the rate of reaction between F₂ and SiO₂ is slow, the rapid formation of SiF₄ is attributed either to atomic F formed in the original decomposition or to decomposition of F₂, which is photosensitive in the wave-length region studied.

^{58b} Cf. Elliot, *Proc. Roy. Soc. (London)*, **127**, 638 (1930); Dixon, *Z. physik. Chem.*, Bodenstein-Festband, 679 (1931).

⁵⁹ Glissman and Schumacher, *Z. physik. Chem.*, **B24**, 328 (1934).

The absorption spectrum of F_2O_2 was measured by Brodersen, Frisch, and Schumacher.⁶⁰ The continuum begins at $\sim 5500 \text{ \AA}$. Several maxima appear. Measurements have been made down to $\sim 3300 \text{ \AA}$, at which point the extinction coefficient is still increasing. Decomposition is presumed to occur in the continuum, but whether it is into $2FO$ or $F_2 + O_2$ cannot be determined with the data at hand. Since, however, previous work has shown that FO has no measurable life, it seems that, if it is formed in the primary step, it yields fluorine and oxygen in a rapid reaction.

7.52 Chlorine monoxide. The absorption spectrum of Cl_2O has been studied over the range $8500\text{--}2200 \text{ \AA}$.⁶¹ The spectrum is entirely continuous. It sets in at $\sim 6600 \text{ \AA}$, and shows definite maxima at 6250 , 5300 , 4100 , and $2560 \text{ \AA}$, the last being very broad and intensive. Decomposition into chlorine and oxygen occurs at all of these wave lengths. On energetic grounds, Finkelnburg, Schumacher, and Stieger have attributed the initiation of the continuum to the elementary act



where the Cl atom may be either in a normal state or in a state with ~ 0.1 e.v. excitation energy (probably the latter).⁶² The intermediate maxima are attributed to the same products in various states of excitation, while the last and most intensive at $2560 \text{ \AA}$ is attributed to the decomposition



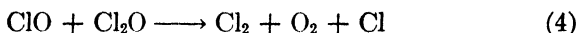
The decomposition rate on illumination is independent of the Cl_2 or Cl_2O pressure or of the presence of foreign

⁶⁰ Brodersen, Frisch, and Schumacher, *ibid.*, **B37**, 25 (1937).

⁶¹ (a) Bodenstein and Kistiakowsky, *Z. physik. Chem.*, **116**, 371 (1925); (b) M.C.F. Goodeve and Wallace, *Trans. Faraday Soc.*, **26**, 254 (1930); (c) Finkelnburg, Schumacher, and Stieger, *Z. physik. Chem.*, **B15**, 127 (1931).

⁶² The reasoning by which Finkelnburg, Schumacher, and Stieger cast out the possibility of $Cl_2O + h\nu \rightarrow Cl_2 + O$ is unconvincing, particularly at the longer wave lengths. ΔH for that reaction is estimated at 36 kcal. , compared with 43 kcal. (i.e., $6500 \text{ \AA}$) for reaction (1).

gases; it depends entirely on the amount of light absorbed at wave lengths of 4360, 3650, and 3130 Å. Since chlorine also absorbs in this region, this means that the rate is independent of whichever compound is the light absorbent. Similarly, the quantum efficiencies at 10°C., for 4360 Å = 3.2, for 3650 Å = 3.4, and for 3130 Å = 3.5 mols per einstein absorbed, are independent of whichever of the two substances is the light absorbent. The reaction must proceed through a chain mechanism involving chlorine atoms. The reaction has a positive temperature coefficient. In order to explain their results, Finkelnburg, Schumacher, and Stieger suggested the chain



Among the intermediate products of reaction, they report ClO_2 and higher chlorine oxides of unknown formula.

The photolysis of Cl_2O between 2350 and 2750 Å was investigated by Schumacher and Townend,⁶³ who report a quantum yield of 4.5 at 20°C. They conclude that reaction (2) occurs, as predicted^{61c} from spectral considerations, and that the Cl atoms take part in chains, as described above; but that neither O atoms nor O_3 molecules react with Cl_2O .

For the photolysis of Cl_2O in solution, see §14.13.

7.53 Chlorine dioxide. The most recent measurements of the absorption spectrum of ClO_2 are by Finkelnburg and Schumacher,⁶⁴ and by Urey and Johnston.⁶⁵ The latter succeeded in analyzing the bands. The spectrum extends from 5225 Å to 2700 Å. The bands show rotational fine structure down to 3753 Å, where they become diffuse. Extrapolation of the measurements indicates that the bands themselves disappear at ~ 2560 Å.

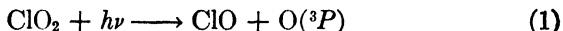
The wave length 3753 Å corresponds to ~ 76 kcal. The decomposition of ClO_2 into atoms requires ~ 122.5 kcal.

⁶³ Schumacher and Townend, *Z. physik. Chem.*, **B20**, 375 (1933).

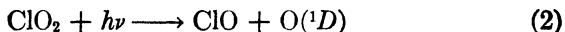
⁶⁴ Finkelnburg and Schumacher, *Z. physik. Chem.*, Bodenstein-Festband, 704 (1931).

⁶⁵ Urey and H. Johnston, *Phys. Rev.*, **38**, 2131 (1931).

If we assume that one atom is held as strongly as another, the dissociation into $\text{ClO} + \text{O}$ will require approximately half as much energy. Therefore it may reasonably be assumed that the predissociation reaction is



Were an excited O atom to be produced, ~ 45 kcal. additional energy would be required, or a minimum total of ~ 106 kcal. ($\frac{1}{2} \times 122.3 + 45$), corresponding to $2670 \text{ \AA}$. Thus it appears that the continuum beginning at $\sim 2560 \text{ \AA}$ corresponds to the primary reaction



As might be expected on the basis of the diffuseness of the spectrum, Murphy⁶⁶ found that no fluorescence was excited in ClO_2 by light of $3060 \text{ \AA}$.

The actual photodecomposition has been studied, principally qualitatively, by a number of investigators.⁶⁷ Booth and Bowen detected the formation of a red liquid which Bodenstein, Hardeck, and Padelt subsequently identified as Cl_2O_6 .⁶⁸ Cl_2 and O_2 are also among the products. Spinks and Porter have studied the photolysis of the moist gas as well as of the dry. In moist gas, the quantum yield is increased from 3.1 at $4360 \text{ \AA}$ to 3.7 at $3650 \text{ \AA}$. When dry ClO_2 is used, Cl_2O_6 is formed and condenses on the walls, undergoing subsequent photodecomposition. At 31°C ., thermal decomposition of Cl_2O_6 , with formation of chlorine and oxygen, is rapid.

According to Spinks and Porter, the following steps, after reaction (1), adequately account for the results obtained:

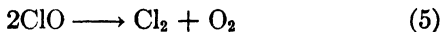


⁶⁶ Cited by Urey and Johnston, *loc. cit.*

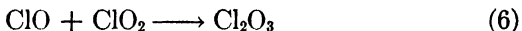
⁶⁷ Bowen, *J. Chem. Soc.*, **123**, 2328 (1923); Booth and Bowen, *ibid.*, **127**, 510 (1925); Bodenstein, Hardeck, and Padelt, *Z. anorg. allgem. Chem.*, **147**, 233 (1925); Spinks, *J. Am. Chem. Soc.*, **54**, 1689 (1932); Spinks and J. M. Porter, *ibid.*, **56**, 264 (1934).

⁶⁸ It is interesting to note that the first recorded synthesis of this substance is by Millon, *Liebigs Ann.*, **46**, 311 (1843).

⁶⁹ According to Byrns and Rollefson, *J. Am. Chem. Soc.*, **56**, 2245 (1934), ClO_3 undergoes a chlorine-sensitized decomposition. Furthermore, the O atoms formed in reaction (1) can react with O_2 , yielding ozone (cf. § 12.3).



There is also the possibility



Hamann and Schumacher⁷⁰ state that reaction (5) has a low energy of activation; it should therefore take place readily at room temperatures. In this way, all the products obtained are accounted for.

The photolysis of ClO_2 in solution is mentioned in § 14.13, and the sensitized decomposition in § 10.66.

7.54 Chlorine trioxide and chlorine hexoxide. Cl_2O_6 was first prepared by Millon.⁶⁸ It has been shown⁷¹ that, in the gaseous state, the oxide exists almost exclusively as ClO_3 . Magnetic measurements⁷² have revealed that, in the liquid and solid states, there is an equilibrium between the two forms ClO_3 and Cl_2O_6 . The concentration of ClO_3 in the mixture increases with temperature; at 10°C ., it amounts to 1 per cent.

The absorption spectra of the two substances were measured by Goodeve and Richardson.⁷³ Liquid Cl_2O_6 was found to absorb strongly from $\sim 6000 \text{ \AA}$ to the limit of the spectrograph at $2200 \text{ \AA}$. Gaseous ClO_3 showed a continuum beginning at $\sim 3500 \text{ \AA}$, and having maxima at $2760 \text{ \AA}$ and beyond $2200 \text{ \AA}$ (perhaps at $\sim 2000 \text{ \AA}$).

Remarks on the photochemistry of these compounds appear in the previous section (§ 7.53).

7.55 Chlorine heptoxide. Goodeve and Windsor⁷⁴ have studied the absorption spectrum of Cl_2O_7 down to $45,000$

Byrns and Rollefson showed that ClO_3 , in addition to decomposing to yield ClO_2 , reacts with O_3 to give Cl_2O_7 , which is relatively inert (see § 7.55). Obviously the mechanism suggested by Spinks and Porter is only a partial picture of the facts.

⁷⁰ Hamann and Schumacher, *Z. physik. Chem.*, **B17**, 293 (1932).

⁷¹ C. F. Goodeve and Todd, *Nature*, **132**, 514 (1933); Goodeve and F. D. Richardson, *J. Chem. Soc.*, 294 (1937).

⁷² Farquharson, Goodeve, and Richardson, *Trans. Faraday Soc.*, **32**, 790 (1936).

⁷³ Goodeve and Richardson, *ibid.*, **33**, 453 (1937).

⁷⁴ C. F. Goodeve and Windsor, *ibid.*, **32**, 1518 (1936).

cm.⁻¹ (2221 Å). The continuum begins at ~ 3100 Å. There is apparently a trend toward a maximum at less than 2200 Å. No photochemical study has been reported.

7.56 Bromine monoxide. Br₂O was synthesized by Brenschede and Schumacher,⁷⁵ and its extinction coefficient was measured in carbon-tetrachloride solution. Its spectrum is continuous from ~ 7500 Å continuing toward the ultraviolet. There is a maximum near 6300 Å and a minimum at 5300 Å. At 4300 Å, which was the limit of observation, the extinction coefficient is still increasing. The photochemistry of Br₂O was studied only in solution. All that can be stated is that the overall decomposition is Br₂O → Br₂ + $\frac{1}{2}$ O₂ and Br₂O + CCl₄ → COCl₂ + Br₂ + Cl₂. It is not a very stable compound, for it decomposes in the dark in a few days according to the same reactions.

Hydrogen Compounds of the Oxygen Family

7.6 Water. The extinction coefficient of liquid water has been measured from the visible down to about 2000 Å.⁷⁶ Near that point the extinction coefficient begins to rise, as shown in Fig. 30a⁷⁷ (p. 172) for water vapor. According to Lyman,⁷⁸ a layer of liquid water 0.5 mm. thick is transparent to light down to 1792 Å. The figures of Kreusler,⁷⁹ as extrapolated by Leifson,⁸⁰ indicate that 1830 Å is the limit of transparency of a liquid water layer 17 mm. thick. According to Price,⁸¹ the vapor displays a continuum at 1785 to 1550 Å. The maximum is at ~ 1700 Å. Beginning at about 1392 Å, there is a region of broad and diffuse bands⁸² extending down to < 1000 Å. The estimated limit corresponds to an ionization potential of 12.56 ± .02 e.v.

⁷⁵ Brenschede and Schumacher, *Z. anorg. allgem. Chem.*, **226**, 370 (1936); *Z. physik. Chem.*, **B29**, 356 (1935).

⁷⁶ Dawson and Hulburt, *J. Optical Soc. Am.*, **24**, 175 (1934).

⁷⁷ Granath, *Phys. Rev.*, **34**, 1045 (1929).

⁷⁸ Lyman, *Nature*, **84**, 71 (1910).

⁷⁹ Kreusler, *Ann. Physik*, **6**, 412 (1901).

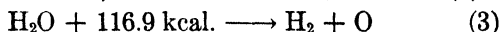
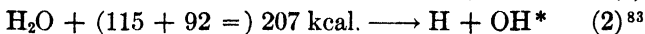
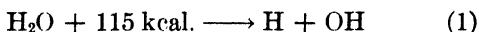
⁸⁰ Leifson, *Astrophys. J.*, **63**, 73 (1926).

⁸¹ W. C. Price, *J. Chem. Phys.*, **4**, 147 (1936).

⁸² Cf. Rathenau, *Z. Physik*, **87**, 32 (1934).

The absorption at the low wave lengths is associated with excitation of a non-bonding electron.

The primary decomposition corresponding to absorption in the continuum may correspond to one of the reactions below:



The wave lengths 1780 Å and 1392 Å correspond to ~ 159 kcal. and ~ 204 kcal. respectively. Thus it appears that both reactions (1) and (3) are energetically possible in either continuum, and that there is a possibility that reaction (2) may occur in the second continuum. The approximate agreement in energies must be regarded as fortuitous. What we know about potential energy curves indicates that in

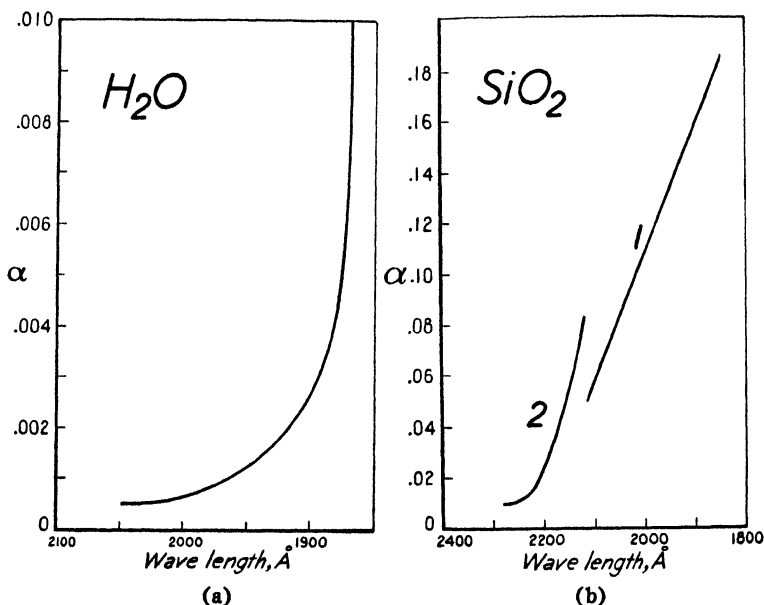
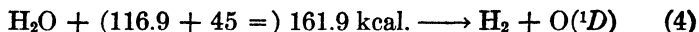


Fig. 30. Extinction Coefficients, according to Granath, *Phys. Rev.*, **34**, 1045 (1929): (a) Water Vapor, saturated at 25°. (b) Quartz. Curve 1 represents values for a 2.5 cm. thickness, and curve 2 values for an 11.7 cm. thickness of crystal quartz. The absorption coefficient α is defined by $I = I_0 \times 10^{-\alpha l}$, where l is expressed in cm.

⁸³ Cf. Terenin and Neujmin, *J. Chem. Phys.*, **3**, 436 (1935).

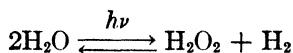
most cases the transition which occurs actually corresponds to an energy change in excess (sometimes considerably in excess) of thermochemical requirements (cf. § 4.8).⁸⁴ It is for such a reason that we cannot accept the idea once expressed⁸⁵ that the reaction



corresponds to the absorption in the first continuum.

To choose between the possible primary steps, we must resort to chemical evidence, of which there is but little.⁸⁶ Kernbaum⁸⁷ obtained hydrogen and hydrogen peroxide by illuminating water with ultraviolet light for ten hours. Coehn⁸⁸ described experiments with irradiated water held at a temperature of 150°C., in which about 0.2 per cent dissociation of water to form H_2 and O_2 was detected in the photostationary state. Coehn and Grote⁸⁹ found that, if a mixture of H_2 and O_2 was passed rapidly through an insulated quartz vessel, H_2O_2 could be detected among the products, but that none was found in either a static experiment or after a *slow* passage. It is possible that H_2O_2 is always formed as an intermediate product and that O_2 results from its subsequent decomposition.

According to Tian,⁹⁰ if water is exposed to light of 1900 Å, a photostationary state of the type



⁸⁴ In the past it was thought that such close agreement had unambiguous significance. Cf. Mecke, *Trans. Faraday Soc.*, **27**, 369 (1931), where this case is discussed according to the ideas then current.

⁸⁵ Cf. C. F. Goodeve and Stein, *Trans. Faraday Soc.*, **27**, 393 (1931).

⁸⁶ Goodeve and Stein, *loc. cit.*, are of the opinion that none of the photochemical work on water (i.e., prior to 1931) is subject to simple interpretation. They doubt the effectiveness of the light sources used below 1950 Å, and attribute the results described to photosensitization either by impurities or by the walls of the containing vessel. They may be correct, but it is noteworthy that no photochemical evidence of any kind on the subject has been produced since 1931. Pending the production of new evidence, the old may be accepted or rejected as the reader chooses. Purely formally, however, it is simpler to reason from a few facts than from none at all; that is the procedure pursued in the following paragraphs.

⁸⁷ Kernbaum, *Compt. rend.*, **149**, 273 (1909).

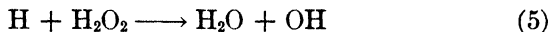
⁸⁸ Coehn, *Ber.*, **43**, 880 (1910).

⁸⁹ Coehn and Grote, *Nernst Festschrift*, Wilhelm Knapp, Halle, 1912, p. 136.

⁹⁰ Tian, *Ann. phys.*, [9] **5**, 248 (1926).

is set up. If dissolved oxygen is present, the latter reacts with hydrogen under the influence of the light and the concentration of H_2 is cut down, with a simultaneous increase in the steady state concentration of H_2O_2 . Simultaneous production of ozone and interaction of that substance with H_2O_2 also introduce complexities.

If it is assumed that all the evidence presented above can be accepted at face value, then it is extremely unlikely that reaction (3) occurs at all. The reaction of atomic oxygen with H_2O_2 is much more rapid than that with H_2 (§ 7.61); presumably it is also far more rapid than that with H_2O . Consequently, were reaction (3) to occur to any considerable extent in the primary step, formation of H_2O_2 could not be detected. However, similar reasoning might be applied to reaction (1). The reaction



is known to take place very rapidly.⁹¹ Yet H_2O_2 has been detected experimentally, although it was not found by Kernbaum in his static reaction. Presumably, in the liquid state the probability of reaction (5) is not great, for there is also a high probability of other reactions involving atomic hydrogen.⁹²

Perhaps the best evidence for reaction (1) as against reaction (3) is in work on the products of the electrodeless discharge in water vapor. Rodebush and Wahl⁹³ proved, by a Stern-Gerlach experiment,⁹⁴ that free O atoms are absent from the gases flowing out of the discharge; they found no molecular oxygen in the discharge itself. When the products of the electrodeless discharge are examined for afterglow,^{93,95} it is found to be exceedingly faint. Its intensity is known to be high if both O and H are present.⁹⁶

⁹¹ Geib, *Z. physik. Chem.*, **A170**, 1 (1934).

⁹² Cf. Rodebush, Wende, and Campbell, *J. Am. Chem. Soc.*, **59**, 1924 (1937).

⁹³ Rodebush and Wahl, *J. Chem. Phys.*, **1**, 696 (1933).

⁹⁴ A Stern-Gerlach experiment involves the passage of a molecular beam through an inhomogeneous magnetic field.

⁹⁵ (a) Stoddart, *Phil. Mag.*, [7] **18**, 410 (1934); (b) Oldenberg, *J. Chem. Phys.*, **3**, 266 (1935).

⁹⁶ Bonhoeffer and Pearson, *Z. physik. Chem.*, **B14**, 1 (1931).

Stoddart ^{95a} found that the addition of oxygen to the water vapor enhanced the afterglow. Hence it is extremely unlikely that atomic O is formed in the electrodeless discharge in the pure vapor. In addition, Oldenberg ^{95b,97} identified OH by its absorption spectrum in the products of the discharge. Presumably the processes occurring in the photochemical decomposition are similar to those in the electrodeless discharge; ⁹⁸ thus it may be concluded that the primary photochemical act is probably



Certainly reaction (1') is to be preferred to reaction (3), on structural considerations alone. Herzberg, ⁹⁹ in criticizing the suggestion of Goodeve and Stein as to reaction (4), pointed out that the hydrogen atoms are not connected in the molecule to begin with, and that consequently a reaction of the type of (1) is more probable.¹⁰⁰

The H_2O_2 reported formed in the photolysis of water might result then from subsequent reactions of H or H_2 and O_2 (cf. § 10.32). Evidence of Rodebush, Wende, and Campbell ⁹² indicates that it is not formed by combination of hydroxyl radicals.

It is clear that the photochemical work thus far performed on water is quite fragmentary and of doubtful validity.

7.61 Hydrogen peroxide. Considering the simplicity of the H_2O_2 molecule, we note that surprisingly little work has been done on its photochemistry. Urey, Dawsey, and Rice¹⁰¹ studied both the pure vapor and the aqueous solution in the range 3800–2150 Å. They state that, for the solution, absorption begins between 3800 and 3700 Å. For the vapor, their photographs showed a continuum without traces of structure, beginning at 3100–3000 Å. Coefficients of absorption were determined, for solution,

⁹⁷ Oldenberg, *J. Phys. Chem.*, **41**, 293 (1937).

⁹⁸ In the electrodeless discharge, however, there is a greater probability of the formation of excited particles in the primary act.

⁹⁹ Herzberg, *Trans. Faraday Soc.*, **27**, 402 (1931).

¹⁰⁰ However, the discussions of various organic compounds in later sections (see Chapter VIII) indicate that there are limitations to this type of reasoning.

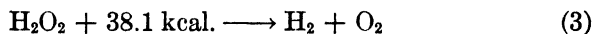
¹⁰¹ Urey, Dawsey, and Rice, *J. Am. Chem. Soc.*, **51**, 1371 (1929).

in the range 3750–2150 Å; for vapor, in the range 2750–2150 Å. Within the limits of experimental error, the two absorption curves were identical over the latter range. It is consequently reasonable to conclude that for the vapor, as for the solution, absorption begins at ~ 3750 Å.

Measurements of the absorption spectra of solutions made by others¹⁰² are in fair agreement with this figure as to the beginning of the continuum in solution; there is, however, considerable disagreement between them and Urey, Dawsey, and Rice as to the extinction coefficients, although the former agree among themselves. Later work by Fergusson, Slotin, and Style¹⁰³ on both vapor and solution has contributed a new set of data on extinction coefficients but has not served to simplify matters. The latter authors prefer their own figures, because of the experimental methods they employed.

Sharma¹⁰⁴ continued the studies to lower wave lengths, using the vapors of aqueous solutions, and found a "sharp cut at 2055 Å,"¹⁰⁵ which he attributed to a transition to a second repulsion curve.

The net photochemical reaction is a decomposition into water and oxygen. The simplest possible primary steps, together with the energies required, are listed below:



The energies required for the first three reactions were calculated from the data of Tables 30 and 31 (Appendix II); the figure for reaction (4) is according to an estimate by

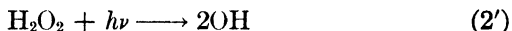
¹⁰² (a) Henri and Wurmser, *Compt. rend.*, **156**, 1012 (1913); *ibid.*, **157**, 126, 284 (1913); *J. phys. rad.*, **3**, 305 (1913). (b) Kornfeld, *Z. wiss. Phot.*, **21**, 66 (1921). (c) Allmand and Style, *J. Chem. Soc.*, 596 (1930).

¹⁰³ Fergusson, Slotin, and Style, *Trans. Faraday Soc.*, **32**, 956 (1936).

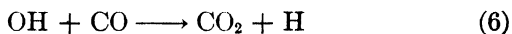
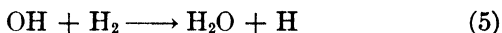
¹⁰⁴ R. S. Sharma, *Proc. Acad. Sci. United Provinces Agra Oudh* (India), **4**, 51 (1934).

¹⁰⁵ This was, presumably, a sharp increase in the extinction coefficient in the continuum.

Bray.¹⁰⁶ Evidently, light of 7400 Å contains enough energy to effect reaction (1) or (3); reaction (2) is energetically possible at wave lengths below ~ 5450 Å. On the other hand, reaction (4) would be expected to require light of ~ 3350 Å or less. It thus appears that, of the four reactions listed, any one of the first three might possibly occur in the first continuum. On the basis of experiments in which a condensed electric discharge was passed through H_2O_2 and the emission spectra of the products studied, Urey and his co-workers¹⁰¹ concluded that light also dissociates H_2O_2 into a normal and an excited OH radical. A fluorescence characteristic of excited OH radicals appeared in experiments at $\lambda = 2138\text{--}2025$ Å. The only products obtained in the photolysis are H_2O and O_2 , and thus reaction (3) is excluded as a possible primary process. As for reaction (1), von Elbe¹⁰⁷ photolyzed H_2O_2 in the presence of H_2 and CO in different experiments, and obtained H_2O and CO_2 from those two substances respectively. The results could not be accounted for on the basis of the primary reaction (1), since the O atoms would be expected to react with H_2O_2 much faster than with hydrogen or carbon monoxide.¹⁰⁸ He proposed, instead, the primary reaction



followed by



to explain his results.¹⁰⁹

It would seem therefore that the products of the photolysis

¹⁰⁶ Bray, *J. Am. Chem. Soc.*, **60**, 82 (1938).

¹⁰⁷ Von Elbe, *J. Am. Chem. Soc.*, **54**, 821 (1932); **55**, 62 (1933). Cf. von Elbe and Lewis, *ibid.*, **54**, 552 (1932).

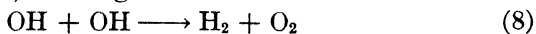
¹⁰⁸ Cf. Kistiakowsky, *J. Am. Chem. Soc.*, **52**, 1868 (1930); Harteck and Kopsch, *Z. physik. Chem.*, **B12**, 327 (1931).

¹⁰⁹ For reaction (6), cf. Bonhoeffer and Haber, *Z. physik. Chem.*, **137**, 263 (1928); Lavin and Jackson, *J. Am. Chem. Soc.*, **53**, 383, 3189 (1931). See also, for similar conclusions as to reaction (2'), Dain and Shvartz, *Acta. Physicochim. U.R.S.S.*, **3**, 219 (1935); *J. Phys. Chem.* (U.S.S.R.), **4**, 478 (1933); **7**, No. 2 (1936).

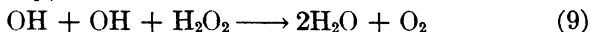
of H_2O_2 might be accounted for by a reaction suggested by Bonhoeffer and Pearson:⁹⁶



However, this is in sharp contradiction to Rodebush, Wende, and Campbell,⁹² who state explicitly that there is no evidence for such a reaction, although the reaction



does take place readily at low pressures as a wall reaction. Inasmuch as hydrogen is not found among the products, it is possible that the secondary reaction is as proposed by von Elbe; namely,



As for the shorter wave lengths, Sharma concludes that H atoms are probably formed, although the experimental evidence is not very convincing.¹¹⁰ It would be helpful, in interpretation of the results, if quantum yield measurements in the vapor state were available over the whole range of studies. Evidently work still remains to be done.

The photolysis of H_2O_2 in solution is discussed in § 14.5.

Other Hydrogen Compounds

7.62 Hydrogen sulfide. The work thus far completed on H_2S is a good illustration of what ought to be done in the case of water (cf. § 7.6). Both its absorption spectrum and its photochemistry have been investigated. The extinction coefficient of H_2S as determined by Goodeve and Stein¹¹¹ is shown in Fig. 31. Continuous absorption begins at ~ 2800 Å. This may be contrasted with the beginning of continuous absorption for water (at ~ 1792 Å) and is in consonance with the lesser stability of hydrogen sulfide.

The photolysis of H_2S into hydrogen and sulfur has been studied by Stein,^{112a} and by Forbes, Cline, and Bradshaw.^{112b} The results of the two investigations differ materially. Whereas the former reports a quantum yield (of H_2S de-

¹¹⁰ Sharma (*loc. cit.*) also considers the possibility of $\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{H} + \text{O}_2$, which requires ~ 140 kcal., corresponding to ~ 2030 Å.

¹¹¹ Goodeve and Stein, *Trans. Faraday Soc.*, **27**, 393 (1931).

¹¹² (a) Stein, *Trans. Faraday Soc.*, **29**, 583 (1933); (b) Forbes, Cline, and Bradshaw, *J. Am. Chem. Soc.*, **60**, 1431 (1938).

composed) at $\sim 2050 \text{ \AA}$, varying from 2.2 for H_2S at 75 mm. pressure to 3.6 at 1350 mm.; the latter report a quantum yield, at $2080 \text{ \AA}$, of $1.02 \pm .05$ (i.e., unity within experimental error) independent of pressure over the range 8 to 1400 mm. and over a fourteen-fold range of light intensity.

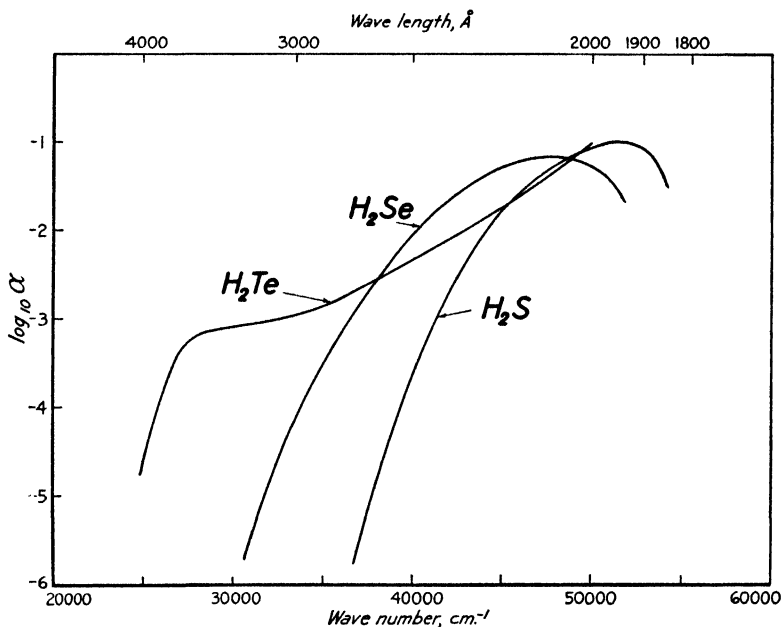
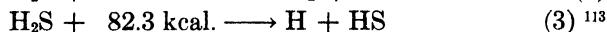
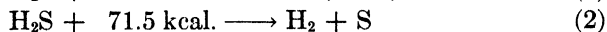
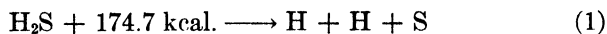


Fig. 31. Extinction Coefficients for Hydrogen Sulfide, Hydrogen Selenide, and Hydrogen Telluride, according to Goodeve and Stein, *Trans. Faraday Soc.*, **27**, 393 (1931). Here α is defined by the equation $\alpha = \frac{1}{pl} \log \frac{I_0}{I}$, where p is in atmospheres and l in cm.

Factors which may have interfered with the accuracy of Stein's work were eliminated by Forbes and his co-workers; their result is doubtlessly the more reliable.

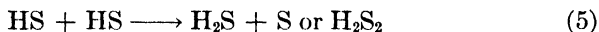
The possible primary reactions are similar to those given in the case of water. They are:



¹¹³ The thermochemical values for reactions (1) and (2) may be calculated from Tables 30 and 31 in Appendix II. The value for reaction (3) is as esti-

Reaction (1) obviously could not occur at 2050 Å. Reaction (2) is energetically possible below ~ 3995 Å, and reaction (3) below ~ 3450 Å. Since the continuum begins at ~ 2750 Å, both these reactions are possible primary steps.^{114a}

The mechanism suggested by Herzberg^{114b} and favored by Forbes and his co-workers is:



The alternative mechanism which would also give a quantum yield of unity under all conditions is:



However, experiments of Avery and Forbes¹¹⁵ on the photolysis of H_2S dissolved in chloromethanes clearly indicate the formation of hydrogen atoms (by their reactions with the solvent); consequently, reactions (3'), (4), and (5) are the probable mechanism in the gaseous state.

7.63 Hydrogen selenide and hydrogen telluride. The extinction coefficients for H_2Se and for H_2Te , as measured by Goodeve and Stein,¹¹¹ are shown together with those of H_2S in Fig. 31. Comparison of the curves with the similar one for water (Fig. 30a) shows a gradually decreasing stability as we pass from H_2O to H_2Te .

The decomposition of H_2Se into normal atoms



obviously cannot proceed in the first continuum. However, the reaction



mated by Stein. However, it might be expected, from analogy to the case of H_2O , that the energy required should be at least half of that for reaction (1); i.e., > 87.4 kcal. or < 3245 Å.

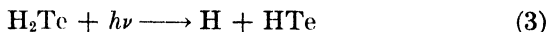
¹¹⁴ (a) Goodeve and Stein, ref. 111, proposed the reaction producing excited sulfur atoms, $\text{H}_2\text{S} + h\nu \rightarrow \text{H}_2 + \text{S}(^1D)$, $\Delta H = 105$ kcal., which becomes energetically permissible below ~ 2705 Å. It is disregarded here for reasons already discussed at length in the case of water (§ 7.6). (b) Cf. Herzberg, *Trans. Faraday Soc.*, **27**, 402 (1931).

¹¹⁵ Avery and Forbes, *J. Am. Chem. Soc.*, **60**, 1005 (1938).

should, by analogy with water (cf. § 7.6), require about half 166 kcal. or ~ 83 kcal., and is consequently energetically possible at 3400 Å.^{115a}

Several investigators,¹¹⁶ including Stein, have reported the decomposition of H₂Se by ultraviolet light. Stein states that red amorphous Se precipitates on the window of the absorption tube.

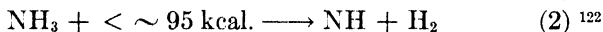
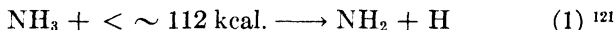
As for H₂Te, no satisfactory thermal data are available. By analogy to the previous cases, the reaction



seems possible.¹¹⁷

7.7 Ammonia. The ultraviolet absorption spectrum of NH₃ has been photographed by Leifson^{33, 118} and by Dixon.¹¹⁹ The latter has catalogued a series of diffuse band maxima extending from ~ 2430 Å to ~ 1950 Å. The diffuse band "centers" measured by Leifson extend from 2260 Å to 1515 Å. Evidently we are here concerned with a phenomenon of predissociation over the entire range studied.¹²⁰

There are only two possible primary reactions:



^{115a} Stein prefers the reaction $\text{H}_2\text{Se} + h\nu \rightarrow \text{H}_2 + \text{Se}(^1D)$.

¹¹⁶ Forcrand and Fonze-Diaczon, *Compt. rend.*, **134**, 171, 229, 281 (1902); Hempel and Weber, *Z. anorg. Chem.*, **77**, 48 (1912); Moses and Doctor, *ibid.*, **118**, 284 (1921).

¹¹⁷ As in the other cases, Stein prefers mechanisms which yield molecular H₂ in the primary act.

¹¹⁸ Cf. Landsberg and Predwotileff, *Z. Physik*, **31**, 544 (1925), who measured the extinction coefficients.

¹¹⁹ Dixon, *Phys. Rev.*, **43**, 711 (1933).

¹²⁰ This statement is not in agreement with the results of Hilgendorff, *Z. Physik*, **95**, 781 (1935), who found eight bands in the region 2007–1765 Å but was unable to find any of the five bands reported by Leifson in the range 1640–1515 Å. Instead, he reported continuous absorption below 1760 Å. However, as will appear below, only the region in which there can be no doubt as to predissociation has been subjected to extensive photochemical investigation. In this connection it may be mentioned that Terenin and Neujmin, *J. Chem. Phys.*, **3**, 436 (1935), observed the emission spectrum of NH₂ when NH₃ was illuminated at < 1650 Å.

¹²¹ See § 10.42, on the photosensitized decomposition of ammonia, for the estimate of ΔH of this reaction.

¹²² See Tables 30 and 31 (Appendix II).

Either of these reactions is energetically possible below 2537 Å. The most recent studies of the photolysis are by Wiig,¹²³ who studied the effect of wave length, of pressure, and of surface area on the quantum yield. The overall reaction under the conditions of his study was determined to be precisely



His results may be summarized by the statement that the quantum yields (of ammonia molecules decomposed per photon absorbed) are generally around 0.25, but depart from that figure in a systematic manner as illustrated in Fig. 32. The quantum yield attains a maximum value of

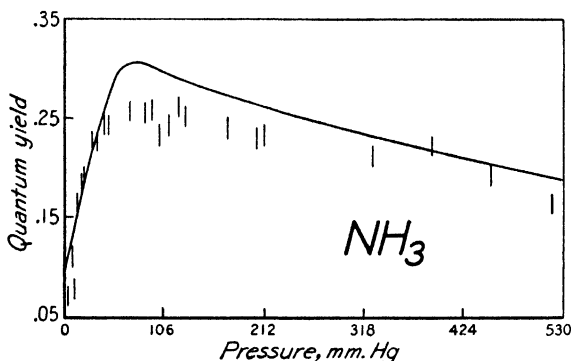


Fig. 32. Quantum Yields in the Photolysis of NH_3 as a function of pressure at $\lambda = 2100 \text{ Å}$, according to Wiig, *J. Am. Chem. Soc.*, **57**, 1559 (1935); **59**, 827 (1937). In the full curve the area:volume ratio = 200 cm^{-1} . The vertical lines are for area:volume ratio = 157 cm^{-1} ; their length is a measure of their error.

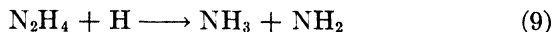
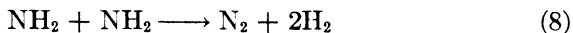
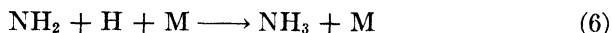
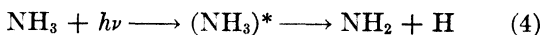
~ 0.32 at about 80 to 90 mm. pressure. At higher pressures it approaches the figure 0.14 reported by Ogg, Leighton, and Bergstrom¹²⁴ for the range 1.2 to 8.5 atmospheres. In the neighborhood of the optimum pressure, increased surface area (as may also be seen from Fig. 32) tends to increase the yield; otherwise, the curve is but slightly

¹²³ Wiig, *J. Am. Chem. Soc.*, **57**, 1559 (1935); **59**, 827 (1937). These papers contain a good bibliography of the previous work.

¹²⁴ Ogg, Leighton, and Bergstrom, *J. Am. Chem. Soc.*, **56**, 318 (1934).

affected. The results of Wiig,¹²³ of Wiig and Kistiakowsky,¹²⁵ of Ogg, Leighton, and Bergstrom,¹²⁴ and of Groth¹²⁶ indicate that change of wave length in the range 1295–2194 Å is without effect on the results.

In order to explain his observations on NH₃, Wiig suggested the mechanism:¹²⁷



The most direct evidence for reaction (4) is that of Geib and Harteck,¹²⁸ who showed that the photochemical products of ammonia could effect the conversion of para to ortho hydrogen and therefore, presumably, contained hydrogen atoms (see § 5.91).¹²⁹

Reactions (5) and (7) are substantiated by the results of Welge and Beckman,¹³⁰ who report only hydrogen and hydrazine as products (and a quantum yield approaching 1.0) when the pressure of products is less than 1 micron, and by the results of others who were able to detect hydrazine in the products by the use of flow methods.¹³¹

Reactions (6) and (9), according to Wiig,¹²³ are supported

¹²⁵ Wiig and Kistiakowsky, *J. Am. Chem. Soc.*, **54**, 1806 (1932).

¹²⁶ Groth, *Z. physik. Chem.*, **B37**, 312 (1937).

¹²⁷ L. Farkas and Harteck, *Z. physik. Chem.*, **B25**, 257 (1934), have suggested a somewhat different mechanism involving the intermediate formation of NH₄. Their conclusions are based mainly on estimates of the atomic hydrogen concentration by the para-ortho conversion method. For remarks on the limitations of this method, *vide infra*.

¹²⁸ Geib and Harteck, *Z. physik. Chem.*, Bodenstein-Festband, 849 (1931).

¹²⁹ According to L. Farkas and Sachsse, *Z. physik. Chem.*, **B23**, 1 (1933); *Trans. Faraday Soc.*, **30**, 331 (1934), any radical containing an odd number of electrons should effect the para-ortho conversion. Thus the result may be due either to NH₂ or to H, but not to NH. Consequently, a reaction of the type of (2) cannot of itself account for this result.

¹³⁰ Welge and Beckman, *J. Am. Chem. Soc.*, **58**, 2462 (1936).

¹³¹ Cf. Bates and Taylor, *J. Am. Chem. Soc.*, **49**, 2438 (1927); Koenig and Brings, *Z. physik. Chem.*, Bodenstein-Festband, 541 (1931); Gedye and Rideal, *J. Chem. Soc.*, 1158 (1932).

by the results of Melville,¹³² who discovered that atomic hydrogen has an inhibiting effect on the rate of the photolysis. Welge and Beckman,¹³⁰ however, maintain that the quantum yield of nearly 1.0, observed by them in the initial stages of the reaction, definitely precludes the possibility of reaction (6). In this they are supported by Mund and van Tiggelen,¹³³ who claim that the rate equations fit the observations more closely if that reaction is ruled out. Wiig is not in agreement with Welge and Beckman as to the quantum yield in the initial stages of the reaction. His measurements extend over a range of product pressures of 0.98 to 2996 microns, and the quantum yields are uniformly low. He offered the suggestion that the difference in light intensities used may account for the difference in results. The observation that NH_2D and NHD_2 are found when mixtures of ammonia, deuterium, and mercury are exposed to a mercury arc¹³⁴ is adequately explained by reaction (9). Direct tests by Dixon¹³⁵ on the reaction between hydrazine and atomic hydrogen are also in support of that step.¹³⁶

Reaction (8), of course, accounts for the production of nitrogen, and proper balancing of the various steps will give the yield of N_2 plus 3H_2 actually observed.

Decrease of pressure from several atmospheres to 100 mm. obviously favors reactions (5)¹³⁷ and (8) as opposed to [(6),] (7) and (9). Wiig¹²³ set up a rate equation for the pho-

¹³² Melville, *Trans. Faraday Soc.*, **28**, 885 (1932).

¹³³ Mund and van Tiggelen, *Bull. soc. chim. Belg.*, **46**, 104, 227 (1937); *Ann. soc. sci. Bruxelles*, Ser. I, **57**, 92 (1937).

¹³⁴ Taylor and Jungers, *J. Chem. Phys.*, **2**, 452 (1934).

¹³⁵ Dixon, *J. Am. Chem. Soc.*, **54**, 4262 (1932).

¹³⁶ Mention should be made at this point that Wenner and Beckman, *J. Am. Chem. Soc.*, **54**, 2787 (1932), studied the photolysis of hydrazine (cf. Koenig and Brings, *loc. cit.*) at 1990 Å, and found quantum yields increasing from 1.0 to 1.7 with increase of pressure over the range 2 to 14 mm. Hg. The mechanism they suggested to explain their results involved a primary step $\text{N}_2\text{H}_4 + h\nu \rightarrow \text{N}_2\text{H}_3 + \text{H}$ and, among others, a secondary step $\text{H} + \text{N}_2\text{H}_4 \rightarrow \text{N}_2\text{H}_3 + \text{H}_2$. The products are nitrogen, hydrogen, and ammonia. According to Imanishi, *Sci. Papers, Inst. Phys. Chem. Research (Tokyo)*, **15**, 166 (1931), the continuum of N_2H_4 begins at ~ 2200 Å.

¹³⁷ Reaction (5) may also occur to a large extent as a three-body collision at high pressures.

tolysis according to the above mechanism and showed that it was in general agreement with the results observed. The low quantum yield at low pressure is attributed to the preponderant effect of wall reactions. The failure to observe any appreciable quantum yield in liquid ammonia¹³⁸ is to be attributed to the almost complete absence of wall reactions and to the preponderance of reactions such as [(6),] (7) and (9). Similarly, (see Fig. 32) the lower observed quantum yield in the reaction cell having relatively smaller surface is to be attributed to the smaller chance of reaction (5) at the intermediate pressures.¹³⁹

7.71 Deutero-ammonia. According to Taylor and Benedict,¹⁴⁰ ND₃ shows absorption beginning at ~ 2300 Å. The principal band at 2136–2139 Å shows a definite structure; at 2105–2122 Å the bands are diffuse. Duncan¹⁴¹ studied the ultraviolet absorption spectra of all the deutero-ammonias from 2200 to 800 Å. He reported that the spectrum of ND₃ above 1675 Å consists of very diffuse bands; below 1675 Å, all the bands are sharp. Between 1675 and 1220 Å, he found two electronic transitions, presumably to stable levels. There was also evidence of a fourth electronic transition below 1220 Å.

Wiig^{140a} showed that the quantum yield in the photolysis of ND₃ is slightly lower than that in the case of NH₃, and that higher quantum yields are obtained in the discrete absorption region at 2138 Å than in the blurred region near 2100 Å. The results are shown in Fig. 33 (p. 186). The latter phenomenon is attributed by Wiig to a mechanism of the type



¹³⁸ Ogg, Leighton, and Bergstrom, *J. Am. Chem. Soc.*, **55**, 1754 (1933).

¹³⁹ The reader is referred to the original paper by Wiig, *J. Am. Chem. Soc.*, **59**, 827 (1937), for a more complete discussion of these points. For example, the results of Warburg, *Sitzb. kgl. preuss. Akad.*, 746 (1911); 216 (1912), which indicate a quantum yield independent of the pressure of added nitrogen or hydrogen within a limited range, are also in line with the mechanism suggested.

¹⁴⁰ Cf. (a) Wiig, *J. Am. Chem. Soc.*, **59**, 955 (1937); (b) Benedict, *Phys. Rev.*, **47**, 641 (1935).

¹⁴¹ Duncan, *Phys. Rev.*, **50**, 700 (1936).

at 2138 Å, which is an example of induced predissociation (see § 4.31) in the discrete absorption region. The increased

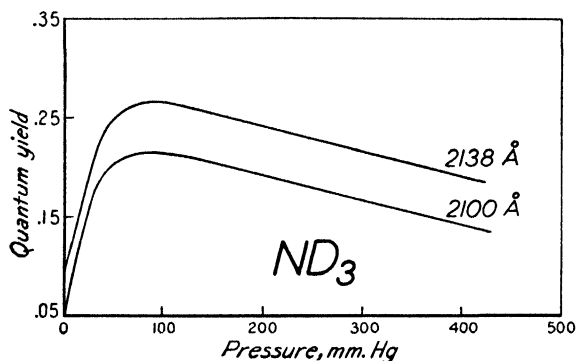


Fig. 33. Quantum Yields in the Photolysis of ND_3 as a function of pressure at $\lambda\lambda = 2138$ and 2100 Å, according to Wiig, *J. Am. Chem. Soc.*, **59**, 955 (1937).

quantum yield at 2138 Å is then attributed to the further possibility of a reaction



which occurs in a small proportion of cases. This suggested mechanism is sufficient to account for the effect observed, for, as in the case of NH_3 , the only reaction to be expected in the diffuse region at 2100 Å is



It is apparently assumed in this mechanism that all the molecules excited in step (10) eventually decompose either by reaction (11) or by reaction (12). The ratio of the amounts disappearing by these reactions is obviously unaffected by pressure. Thus the quantum yield of reaction (12), which is a primary process, is not affected by pressure and is a constant, γ_{12} . However, the ultimate yield of the products formed via step (11) is seriously affected by pressure, according to the mechanism described in the section on ammonia (§ 7.7); and the quantum yield of ammonia molecules decomposed in this way is a function of pressure, $\gamma(p)$. It is consequently evident that the total quantum

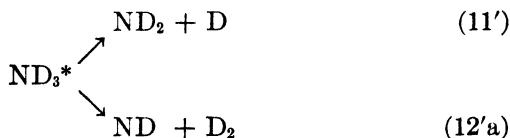
yield consists of two parts: a constant part, responsible for the added quantum efficiency at 2138 Å; and a variable part.

$$\gamma_{2138} = \gamma_k + \gamma(p)$$

This reasoning explains the almost constant vertical distance between the two quantum yield curves in Fig. 33.

The weakness of this mechanism lies in the tacit assumption that all the ND₃ molecules excited in reaction (10) eventually enter reaction (11) or (12). Inasmuch as the sharp structure of the 2138 Å band is ascribed to induced predissociation, fluorescence must be expected in variable amount if steps like (11) and (12) are responsible for the decomposition. The effect would be to decrease the quantum yields of reactions (11) and (12) to extremely low values at low pressures. As has already been repeatedly mentioned, spontaneous predissociation is not necessarily accompanied by diffuseness of a band (see § 4.34). It is possible that the discrete band absorption at 2138 Å results in spontaneous predissociation and that the results reported by Wiig are attributable to some other cause. This appears more likely in view of the improbability of a reaction such as (12). As a general rule, it may be stated that reactions involving four molecules either as reactants or as products proceed extremely slowly (cf. § 5.8).

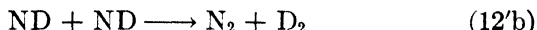
A mechanism which avoids these difficulties has been proposed by Burton.^{141a} It is suggested that the ND₃* molecules formed in reaction (10) on illumination at 2138 Å have a life which is long relative to those formed in the diffuse region at 2100 Å but eventually decompose spontaneously^{141b} by the competing reactions



^{141a} Burton, *J. Chem. Phys.*, **6**, 680 (1938).

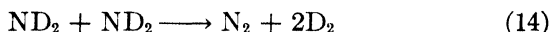
^{141b} Cf. Burton and Rollefson, *ibid.*, **6**, 416 (1938); Rollefson and Burton, *ibid.*, **6**, 674 (1938).

The ND formed in reaction (12'a) is assumed to undergo the reaction



i.e., the quantum yield via (12'a) would be unity independently of pressure; whereas the products of reaction (11') are subject to the pressure effects already discussed. At 2100 Å, only reaction (11') occurs. It may be seen that this mechanism will explain all of Wiig's observations.

Melville¹³² showed that the photolyses of NH₃ and ND₃ are inhibited about equally by both hydrogen and deuterium atoms. The smaller quantum yield in the ND₃ decomposition is to be attributed to the decreased rate of



as compared with reaction (8), a result in general agreement with previous experience in the kinetics of hydrogen and deuterium compounds.

Other mention of the photochemistry of ammonia may be found in the chapters on photosensitization (§ 10.42) and the liquid state (§ 14.13).

7.72 Phosphine. According to Melville¹⁴² the absorption spectrum of phosphine at atmospheric pressure consists of four very weak, diffuse absorption bands at wave lengths of 2360, 2320, 2295, and 2280 Å, followed by a continuum extending from 2250 Å to the limit of observation at 1850 Å. No structure was observable in the diffuse region in spite of the high dispersion of his instruments.¹⁴³

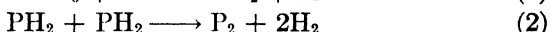
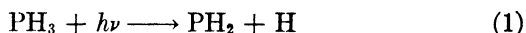
Melville and his co-workers¹⁴⁴ also studied the photolysis of PH₃ and PD₃ at various temperatures and pressures both at an average wave length of 2100 Å (zinc-spark illumination) and in the full light of the mercury arc. Using the quantum yield of the ammonia decomposition as a

¹⁴² Melville, *Proc. Roy. Soc. (London)*, **A139**, 541 (1933).

¹⁴³ A reported disappearance of the diffuse bands at 300°C., as compared with room temperature, is perhaps to be attributed to the fact that he used a much shorter absorption cell at the high temperatures. Increase of temperature shifts the continuum slightly toward the red.

¹⁴⁴ (a) Melville, *Nature*, **129**, 546 (1932); *Proc. Roy. Soc. (London)*, **A139**, 541 (1933); (b) Melville, Bolland, and Roxburgh, *ibid.*, **A160**, 406 (1937).

standard, Melville concluded, on the basis of direct measurement, that the quantum yield of PH_3 decomposition (into red phosphorus and hydrogen) is ~ 0.50 at temperatures up to 300° . However, the assumption was made that the quantum yield of ammonia decomposition is 0.25 at 100 mm. pressure. The more recent measurements of Wiig (see § 7.7) show that the value for the latter depends on the surface-to-volume ratio. It thus appears that the best value for phosphine decomposition, on the basis of Melville's own data, is somewhat less than 0.50 molecules of phosphine decomposed per quantum absorbed. This value is independent of pressure and of the light source used. For PD_3 , the quantum yield is 1.10 times as great with a zinc-spark light source and 1.05 times as great with a mercury-arc source. Melville, Bolland, and Roxburgh^{144b} suggest a mechanism of the type:



Reference to § 7.7 shows both resemblance and contrast to the mechanism found necessary to explain the ammonia photolysis. It is possible that further work on this system may show that its interpretation has been oversimplified. A correctly revised value for the quantum yield of phosphine may not be in so close agreement with the mechanism suggested as the unrevised value (0.50).^{144b} It would be interesting also to obtain information in the region of the diffuse bands; such results would be more directly comparable with those in the ammonia case and would consequently assist interpretation.

7.8 Hydrogen halides. Although four regions of continuous absorption are known for gaseous hydrogen chloride;³³ namely, at 2150 to 1850 Å, 1750 to 1650 Å, 1580 to 1290 Å, and 1270 to 1240 Å, only a slight net decomposition has been observed at these wave lengths,¹⁴⁵ because of

¹⁴⁴ Coehn and Wassiljewa, *Ber.*, **42**, 3183 (1909); Berthelot and Gaudechon, *Compt. rend.*, **156**, 889 (1913).

the rapidity of the back reaction. The different absorption regions have not been fully interpreted. They doubtlessly correspond to various electron jumps to repulsion curves, which lead to a normal hydrogen atom and a chlorine atom in a ^2P state.

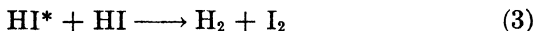
Working at several wave lengths with hydrogen bromide and hydrogen iodide, Warburg¹⁴⁶ measured the amount of reaction per calorie of radiation absorbed. When recalculated on the basis of quantum theory, it is found that two mols were decomposed per einstein absorbed at 2070, 2530, and 2820 Å, within the limits of experimental error (about 5 per cent).¹⁴⁷

7.81 Hydrogen iodide. For the sake of convenience and because it has been so thoroughly studied, we shall consider only hydrogen iodide in this discussion. The case of hydrogen bromide is quite analogous. Both are decomposed into their elements, and there is no appreciable back reaction at room temperature.

Warburg considered that the primary reaction is



Stern and Volmer,¹⁴⁸ on the other hand, suggested what seemed a very plausible mechanism; namely,



The latter mechanism has been rejected on a large variety of grounds, which are summarized below.

(1) Bodenstein and Lieneweg¹⁴⁹ found that the same quantum yield was obtained in the presence of nitrogen up to 3.5 atmospheres, or at temperatures from 150° to 175°. If the activation process (2) actually occurred, then it would be expected that a considerable number of the HI molecules would be deactivated by the nitrogen before they

¹⁴⁶ Warburg, *Sitzb. kgl. preuss. Akad. Wiss.*, 314 (1916); *ibid.*, 300 (1918).

¹⁴⁷ The experiments with the hydrogen halides in water and hexane as solvents are discussed in a later chapter (§ 14.21).

¹⁴⁸ Stern and Volmer, *Z. wiss. Phot.*, **19**, 275 (1920).

¹⁴⁹ Bodenstein and Lieneweg, *Z. physik. Chem.*, **119**, 123 (1926).

could collide with another HI molecule. Of course, it could be pleaded that the nitrogen is ineffective in such deactivation. Their further results that $\gamma = 1.84$ in liquid HI at 3000 Å might be due to special effects in the liquid state.¹⁵⁰

(2) Bonhoeffer and Steiner,¹⁵¹ working on HI, and Tingey and Gerke,¹⁵² working on both HI and HBr, found no trace of structure in the absorption spectrum of either gas. Since the molecules are simple, such a result indicates the direct dissociation of the absorbing molecule in the primary step.

(3) Lewis¹⁵³ found that the quantum yield remains unchanged down to 0.1 mm. In the light of the work of Bodenstein and Lieneweg, it must accordingly be concluded that change of pressure is without effect on the photolysis. If the Stern-Volmer mechanism were correct, a much lower yield would have been obtained at the low pressures, since the mean life of an activated HI molecule (presumably $\sim 10^{-7}$ sec.) would then be much less than the mean time between collisions.

(4) Bonhoeffer and Farkas¹⁵⁴ made tests with streaming HI gas exposed to ultraviolet at .0075 to 2 mm. pressure and found no detectable fluorescence. If the Stern-Volmer theory holds, some fluorescence would have been detected, for here again the mean time between collisions is greater than the period required for spontaneous emission of the energy of activation, as may be estimated from the absorption coefficients (§ 3.22).

(5) In agreement with Lewis's results, Bonhoeffer and Farkas further found that the quantum yield was unchanged at .0075 mm. pressure.

(6) Bonhoeffer and Farkas attributed a fall of pressure, occurring during the photolysis at low pressure, to the

¹⁵⁰ Cf. the discussion of the Franck-Rabinowitch hypothesis (§ 14.11).

¹⁵¹ Bonhoeffer and Steiner, *Z. physik. Chem.*, **122**, 287 (1926).

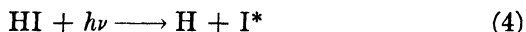
¹⁵² Tingey and Gerke, *J. Am. Chem. Soc.*, **48**, 1838 (1926).

¹⁵³ B. Lewis, *Proc. Nat. Acad. Sci.*, **13**, 720 (1927); *J. Phys. Chem.*, **32**, 270 (1928).

¹⁵⁴ Bonhoeffer and Farkas, *Z. physik. Chem.*, **132**, 235 (1928).

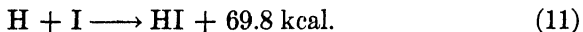
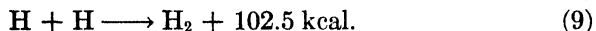
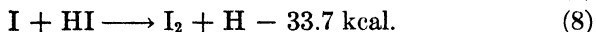
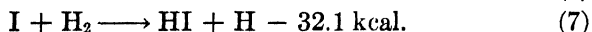
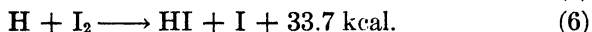
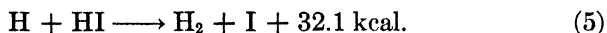
absorption of free atoms on the walls of the containing vessel. A similar effect was obtained with HBr. Their experiments with solid HI and HBr were perhaps the most conclusive, for they were able to absorb the H atoms, detached from the solid surfaces, on a quartz surface cooled with liquid air.

For some time there was also a question as to whether the primary process is necessarily



Rollefson and Booher,¹⁵⁵ working on HI, and Datta,¹⁵⁶ working on both HI and HBr, found that continuous absorption begins at much longer wave lengths than had been previously suspected. Dissociation into normal atoms probably occurs in the initial step at the longer wave lengths; both processes may occur at the short wave lengths. According to Datta, the continuum begins at 4040 Å for hydrogen iodide and at 3260 Å for hydrogen bromide, corresponding to energies of 70.8 and 87.7 kcal. respectively. The heats of dissociation into normal atoms are known to be 69.9 and 85.8 kcal.¹⁵⁷

As for the possible subsequent reactions by which the quantum yield of 2 is explained, the reasoning is simple. The possible reactions, together with the known heats of reaction, are given below:



Since the reaction is studied only in its initial states, when the amount of product is very small, reaction (6) cannot occur to any appreciable extent. Neither does reaction (7),

¹⁵⁵ Rollefson and Booher, *J. Am. Chem. Soc.*, **53**, 1728 (1931).

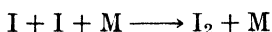
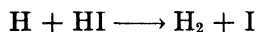
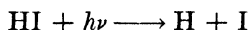
¹⁵⁶ Datta, *Z. Physik*, **77**, 404 (1932).

¹⁵⁷ See Table 31 (Appendix II).

both for that reason and because it is highly endothermic and consequently has an energy of activation of at least 32.1 kcal., which would make reaction improbable at ordinary temperatures even were the concentrations suitable. Reaction (8) does not occur to any appreciable extent for the same reason; its energy of activation is too high.

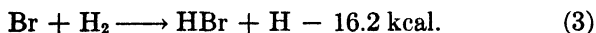
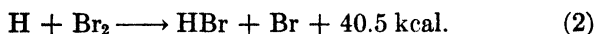
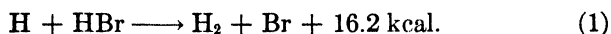
In the section on the reactions of atoms and radicals (§ 5.5), it has been shown that reactions such as (9), (10), and (11) occur only as three-body processes. Furthermore, the rates are decreased by the fact that the atom concentrations attained are always very low. Since atomic hydrogen may disappear readily via reaction (5), the probability of reactions (9) and (11) is extremely small. On the other hand, atomic iodine cannot disappear by any other process; consequently, reaction (10) is the path by which it disappears.

The course of the photolysis is (1), (5), (10):

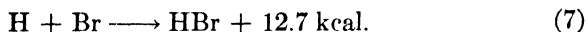
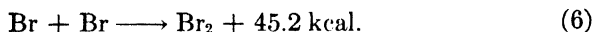
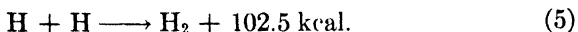
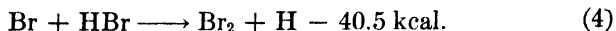


thus completely accounting for the quantum yield = 2. If the photolysis were permitted to proceed far enough, it might be expected that the back reaction (6) would become significant or that the presence of added iodine would inhibit the reaction. Such was indeed found to be the case both by Bodenstein¹⁵⁸ and by Bonhoeffer and Farkas;¹⁵⁴ but whether the observed result was due to reaction (6) or to an *internal filter effect* of the iodine vapor cannot be definitely stated, for the iodine absorbs in the photoactive region.

7.82 Hydrogen bromide. The discussion of the hydrogen iodide case (§ 7.81) applies equally well here. The heats of reaction of the possible reactions concerned are:



¹⁵⁸ Bodenstein, *Trans. Faraday Soc.*, **21**, 525 (1926).



The reader will see that a similar course of reasoning applies here.

7.9 Alkane analogs. For the purpose of this discussion we include in this class not only the silanes and germane but also diborane.

7.91 Silanes. According to Emeleus and Stewart,¹⁵⁹ monosilane, SiH_4 , shows no absorption down to 1850 Å at pressures of 75 mm.; disilane, Si_2H_6 , begins to absorb at 2020 Å at a pressure of 65 mm.; trisilane, Si_3H_8 , at 2190 Å at a pressure of 60 mm. SiH_4 does not undergo unsensitized photolysis in the light of the mercury arc or the condensed aluminum spark,¹⁵⁹ whereas Si_2H_6 and Si_3H_8 were decomposed by Schwarz and Heinrich,¹⁶⁰ using the mercury arc as a light source. The products were free hydrogen and brown deposits with the empirical formulae $\text{SiH}_{1.3}$ and $\text{SiH}_{1.7}$ respectively. Emeleus and Stewart have shown that SiH_4 may be decomposed in a photosensitized reaction in the presence of mercury vapor by the Hg line 2537 Å, yielding hydrogen and a solid, SiH_x (where $x < 0.9$).¹⁶¹ The explosive photo-oxidation of SiH_4 on illumination with the Al spark, the hot mercury arc, or the mercury resonance arc is attributed by Emeleus and Stewart to photoactivation of the oxygen (see § 10.32), since the silane itself is not affected in the wave-length range employed. The radical SiH_2 is presumed to be one of the chain carriers.

7.92 Germane. GeH_4 shows no banded absorption down to the limits of investigation at 1550 Å. Continuous absorption begins at ~ 1700 Å and extends to shorter wave lengths.¹⁶²

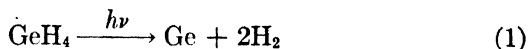
¹⁵⁹ H. J. Emeleus and K. Stewart, *Trans. Faraday Soc.*, **32**, 1577 (1936).

¹⁶⁰ Schwarz and Heinrich, *Z. anorg. allgem. Chem.*, **221**, 277 (1935).

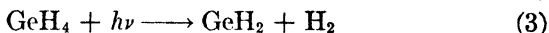
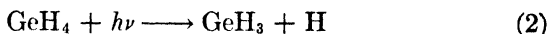
¹⁶¹ For a discussion of reactions photosensitized by mercury vapor, see Chapter X, §§ 10.3 et seq.

¹⁶² Mahneke and Noyes, *J. Am. Chem. Soc.*, **57**, 456 (1935).

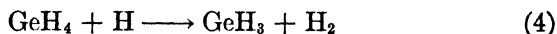
Germane is decomposed by light transmitted by thin layers of quartz, yielding germanium and hydrogen¹⁶³ according to the overall reaction



Mahncke and Noyes¹⁶² indicated that of the two possible primary reactions



they were inclined to favor reaction (2) followed by decomposition of GeH_3 into Ge plus $\frac{3}{2}\text{H}_2$, either in the gas phase or on the walls. Efforts to detect atomic hydrogen in this reaction by the use of the para-ortho hydrogen conversion (cf. § 5.91) were unsuccessful. This result was attributed by Mahncke and Noyes to the rapidity of the reaction



Tests on the photolysis of ammonia in the presence of germane indicated that such a reaction probably occurred.

In the mercury photosensitized decomposition of germane (see § 10.31) the products were found to be the same as in the simple photolysis.¹⁶³

7.93 Diborane. Continuous absorption in the ultraviolet absorption spectrum of B_2H_6 begins at $\sim 2000 \text{ \AA}$ and extends to $1550 \text{ \AA}$. There is a maximum at $1980 \text{ \AA}$, and there is also evidence of another continuum beginning at $\sim 1700 \text{ \AA}$. Presumably there are two superimposed continua corresponding to transitions to two different excited states.¹⁶⁴ Blum and Herzberg have attempted to interpret the various electronic states involved.¹⁶⁵ No photochemical studies have been reported.

¹⁶³ Romeyn and Noyes, *J. Am. Chem. Soc.*, **54**, 4143 (1932).

¹⁶⁴ Blum and Herzberg, *J. Phys. Chem.*, **41**, 91 (1937).

¹⁶⁵ Cf. comments by Mulliken, *ibid.*, **41**, 305 (1937).

CHAPTER VIII

PHOTOLYSIS OF VAPORS OF CARBON COMPOUNDS

8.1 Hydrocarbons. Very little can be said of the photochemistry of the alkanes for the simple reason that they do not absorb light in a conveniently accessible region. On the other hand, the photochemistry of unsaturated hydrocarbons has been rather extensively studied.

8.11 Methane. At atmospheric pressures in a layer 15 mm. thick, methane appears to absorb continuously below 1800 Å.¹ However, when the pressure is reduced to ~ 6 mm., six diffuse bands appear at wave lengths ranging from 1558 to 1420 Å.² Photographs taken under great dispersion and high resolving power³ show a barely detectable, structureless band extending from ~ 1300 to 1200 Å at 0.002 mm. pressure. At 1.0 mm. pressure, apparently continuous absorption begins at 1450 Å and extends to 850 Å, the limit of sensitivity of the apparatus used. In the region 6000–1965 Å, neither methane nor butane shows any absorption at pressures of 40 to 80 cm., in layers 99.95 cm. thick.⁴

The photolysis of methane has been investigated by Leighton and Steiner,⁵ and by Groth and Laudenklos.⁶ The former, using a hydrogen discharge tube as the light source, report an effective radiation near the limit of transmission of fluorite with a quantum yield, based on molecules decomposed per quantum absorbed, crudely estimated to be

¹ Leifson, *Astrophys. J.*, **63**, 87 (1926).

² Rose, *Z. Physik*, **81**, 758 (1933), was unable to confirm this result and attributed the bands to irregularities in the light source used.

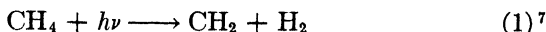
³ Duncan and Howe, *J. Chem. Phys.*, **2**, 851 (1934).

⁴ Kemula and St. Mrazek, *Compt. rend.*, **195**, 1004 (1932).

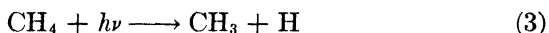
⁵ P. A. Leighton and Steiner, *J. Am. Chem. Soc.*, **55**, 1823 (1933).

⁶ (a) Groth and Laudenklos, *Naturwissenschaften*, **24**, 796, 828 (1936); (b) Groth, *Z. physik. Chem.*, **B38**, 366 (1937).

of the order of unity. Among the products, they identified hydrogen and unsaturated hydrocarbons (assumed to be ethylene), and concluded that the decomposition

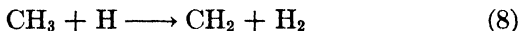
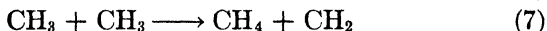
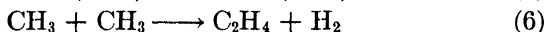
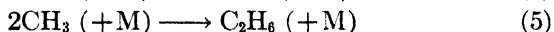


could *not* be the only process involved. Groth and Laudenklos, on the other hand, working with the 1469 and 1295 Å lines of a Harteck xenon lamp and with layers of methane 30 mm. thick and at atmospheric pressure, found H_2 and C_2H_2 as main decomposition products, some C_2H_6 , traces of C_2H_4 , and other hydrocarbons containing three to five carbon atoms. They estimated that 1.30 ± 0.05 moles of hydrogen were formed per quantum absorbed. They stated that some of the methyl radicals react to give C_2H_2 and the other products, and considered the primary reaction to be



which, on energetic grounds, is just as possible as reaction (1) at the wave lengths employed in the photolysis.⁸

Groth^{6b} indicated that the relatively large distances of the H atoms from each other in the CH_4 molecule, as contrasted with the H_2 molecule, is a point in favor of the probability of reaction (3). Various possible secondary reactions, such as

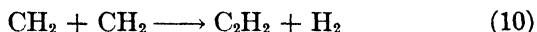


were suggested, but the evidence was not such as to permit a definite choice. However, it may be seen from the work of Spence and Wild on acetone (cf. § 8.76) that in that case, where there are no hydrogen atoms present, ethylene is not

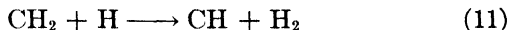
⁷ Cf. Kemula and Dyduzynski, *Roczniki Chem.*, **17**, 423 (in German, 430) (1937).

⁸ See Table 32 (Appendix II).

formed. Consequently it may be concluded that reactions (6) and (7) are extremely improbable, at least at temperatures up to 100°. Ethylene may also be formed, however, from reaction (2), which competes with either



or the successive reactions

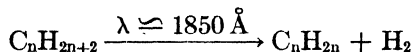


The absence of C_2H_2 among the products of the photolysis of ketene (§ 8.76) may be cited against reaction (10).

As will appear in § 13.21, the products reported by Groth and Laudenklos may result from subsequent decomposition of C_2H_4 . Much more information is required before this problem can be settled.

8.12 Ethane. At very low pressures (0.01 mm.), the absorption spectrum of ethane shows extremely diffuse bands beginning at 1350 Å and extending below 1000 Å. As in the case of methane, the low-pressure bands increase in width as the pressure is increased; at higher pressures, they extend to a limiting value of 1500 Å.⁹ The diffuseness of the bands indicates an unstable upper state.

Kemula and Dydzyszynski⁷ state that, when C_2H_6 , C_3H_8 , and C_4H_{10} are exposed to the light of a mercury arc, the decomposition can be represented by the reaction



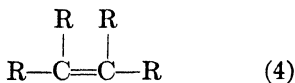
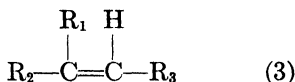
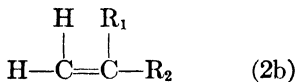
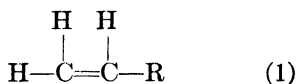
In addition to the unsaturated hydrocarbons, polymers of unknown composition are also formed. No other photochemical investigations of the higher alkanes appear to have been conducted.

8.13 Other aliphatic hydrocarbons. The photochemistry of ethylene is concerned, not only with its absorption spectrum and photolysis, but also with its reactions with hydrogen and its polymerization, both simple and sensitized.

⁹ Price, *Phys. Rev.*, **47**, 444 (1935); cf. Scheibe and Grieneisen, *Z. physik. Chem.*, **B25**, 52 (1933).

Since so many complications are involved, its discussion is better reserved for a later section (§13.21), to which the reader may refer at this point, however, for a description of the absorption spectrum.

The ultraviolet absorption spectra of a large number of other alkenes have been measured and compared by Carr and her co-workers.¹⁰ When the various alkenic hydrocarbons are classified in groups according to structure, it is found that there is a certain regularity in the position of the first band in the Schumann region. The groups are:



The regularity is revealed in Fig. 34. Other features of regularity and irregularity are discussed in the original papers, to which the reader is referred.

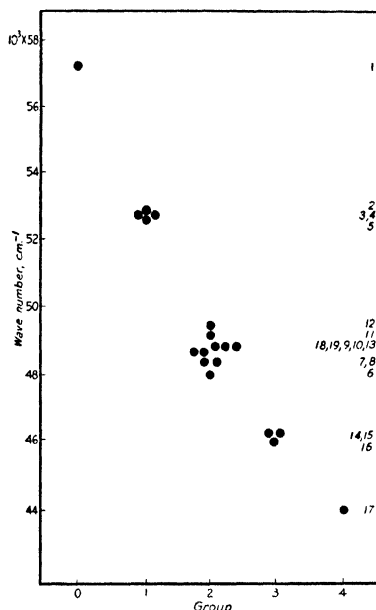


Fig. 34. Positions of the First Bands of the Alkenes, according to Carr and Stücklen, *J. Chem. Phys.*, **4**, 760 (1936): (1) Ethylene. (2) Butene-1. (3) Pentene-1. (4) Heptene-1. (5) Isopropylethylene. (6) *Cis*butene-2. (7) *Trans*butene-2. (8) Pentene-2. (9) Hexene-3. (10) Heptene-3. (11) Isobutene. (12) *Trans*methylethylethylene. (13) Diisobutylene I. (14) Trimethylethylene. (15) Diethylmethylethylene. (16) Diisobutylene II. (17) Tetramethylethylene. (18) Benzene. (19) Diphenyl.

¹⁰ Carr and M. K. Walker, *J. Chem. Phys.*, **4**, 751 (1936). Carr and Walter, *ibid.*, **4**, 756 (1936). Carr and Stücklen, *ibid.*, **4**, 760 (1936); **6**, 55 (1938).

As in the case of ethylene, the photochemistry of acetylene is also more appropriately reserved for a later discussion (§ 13.22).

8.14 Benzene. The absorption spectrum of benzene has been studied repeatedly.¹¹ Sharp band structure begins at $\lambda = 2667 \text{ \AA}$ ($37,494 \text{ cm.}^{-1}$) and extends to $\sim 2200 \text{ \AA}$.¹² A fluorescence which extends to longer wave lengths may be excited in this region. No decomposition is observed. An energy level diagram has been suggested by Kistiakowsky and Solomon to explain the spectrum actually observed. Below $2200 \text{ \AA}$, a number of diffuse bands appear. As is apparent from Fig. 35, the diffuse bands seem to lie on a continuous background, which becomes prominent at about

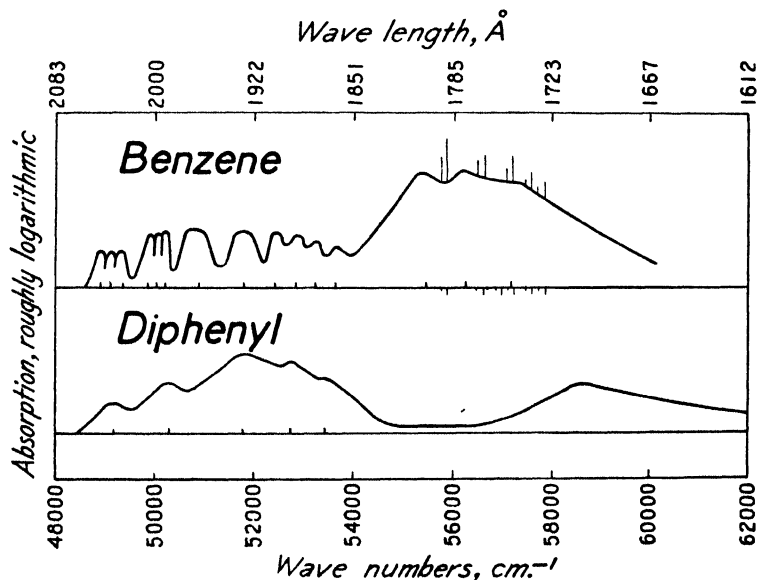


Fig. 35. Diagrammatic Representation of the Absorption Spectra of Benzene and Diphenyl below $2083 \text{ \AA}$, according to Carr and Stücklen, *J. Chem. Phys.*, **4**, 760 (1936).

¹¹ Cf. Henri, *J. phys. rad.*, [6] **3**, 181 (1922); *Structure des Molecules*, Hermann et Cie., Paris, 1925, pp. 108 et seq. Carr and Stücklen, *Z. physik. Chem.*, **B25**, 57 (1934); *J. Chem. Phys.*, **4**, 760 (1936). Price and Wood, *ibid.*, **3**, 439 (1935). Kistiakowsky and Solomon, *ibid.*, **5**, 609 (1937).

¹² See Fig. 35 for a comparison with alkenes and diphenyl.

1850 Å and extends to the limit of observation. Bands at 1789–1732 Å are discernible above the background.

The blurred region from 2200 Å down presumably corresponds to predissociation. Increase of temperature to 330° extends the blurred region to 2400 Å. The continuum presumably corresponds to dissociation, but no photochemical investigations have been reported. Bates and Taylor¹³ reported a very slight decomposition of C₆H₆ in the light of a mercury arc in a photolysis *not* sensitized by Hg vapor; the smallness of the yield precluded analysis. West¹⁴ was unable to detect photodecomposition by the para-ortho hydrogen conversion method (cf. § 5.6), but he used light mainly of 2537 Å. Work ought to be done at lower wave lengths.

8.15 Diphenyl. The absorption spectrum of diphenyl¹⁵ is compared with that of benzene in Fig. 35. All the bands below 2200 Å are diffuse, corresponding to predissociation. A continuum begins about 1785 Å. No photochemical studies are reported.

8.16 Other aromatic hydrocarbons. For data on the absorption spectra of a number of aromatic hydrocarbons, the reader is referred to papers by Hillmer and Schoming,¹⁶ and by Mayneord and Roe.¹⁷ There are no reports on photochemical studies of these compounds in the pure condition.

The polymerization of anthracene is discussed in § 13.3.

8.2 Alkyl halides. The alkyl halides have been subjected to extensive investigation because their structure is simple and well understood,¹⁸ because in this way a regular and well-organized series of compounds may be studied, and because the results obtained consequently should be

¹³ Bates and H. S. Taylor, *J. Am. Chem. Soc.*, **49**, 2438 (1927).

¹⁴ West, *ibid.*, **57**, 1931 (1935).

¹⁵ Carr and Stücklen, *J. Chem. Phys.*, **4**, 760 (1936). Cf. Pickett, Walter, and Prince, *J. Am. Chem. Soc.*, **58**, 2296 (1936), for substituted diphenyls.

¹⁶ Hillmer and Schoming, *Z. physik. Chem.*, **A168**, 81 (1934).

¹⁷ Mayneord and Roe, *Proc. Roy. Soc. (London)*, **A158**, 634 (1937).

¹⁸ Cf. Kronig, *The Optical Basis of the Theory of Valency*, Cambridge University Press, 1935, pp. 29 et seq.

readily interpretable. Fig. 36 shows how the beginning of the continuum shifts toward the visible, with change of the halogen from chlorine to iodine in the case of the methyl halides. This is as might be expected from our knowledge of the strengths of the various carbon-halogen bonds.¹⁹

Very little of the data available on these compounds is really quantitative. As a result, there is disagreement both as to the beginning of the continuum and as to the positions of the absorption maxima in many cases. Table 12 (pp. 204–205) gives a resume of some available data. Hukumoto²⁰ suggests, quite plausibly, that disagreement as to the beginning of a continuum is perhaps to be attributed to the fact that the long wave absorption shades off so gradually that it is difficult to estimate its beginning. In tables which he has compiled, he prefers to emphasize the position of the maximum. As for disagreements about the latter, it is well to point out that only in a few cases (e.g., the work of Porret and Goodeve²¹ on several iodides and bromides) have extinction coefficients actually been measured. Estimates of maxima founded on the appearance of a plate have only limited accuracy.²²

In spite of the disagreements, it may be seen from Table 12 that in general the beginning of the continuum shifts in a regular way toward the red as we proceed through the chlorides, bromides, and iodides, and also as the number of halogen atoms attached to a single carbon atom increases. Generally this shift toward the red may be presumed to be associated with a weakening of the carbon-halogen bond.

As may be seen from Fig. 36, the absorption systems are considerably more extensive and complicated than can be conveniently indicated in Table 12. There is evidence of fine structure for all three methyl halides. Price,²³ for example, extended the work on CH_3I to 1200 Å, found predis-

¹⁹ The bond strengths for Cl, Br, and I amount to 73, 59, and 44 kcal. respectively, according to Kohlrausch, *Der Smekal-Raman-Effekt*, Julius Springer, Berlin, 1931.

²⁰ Y. Hukumoto, *Phys. Rev.*, **42**, 313 (1932); *J. Chem. Phys.*, **3**, 164 (1935).

²¹ Porret and Goodeve, *Trans. Faraday Soc.*, **33**, 690 (1937); *Proc. Roy. Soc. (London)*, **165**, 31 (1938).

²² Cf. Sen-Gupta, *J. University of Bombay*, **5**, Part II (1936).

²³ Price, *Phys. Rev.*, **47**, 419 (1935).

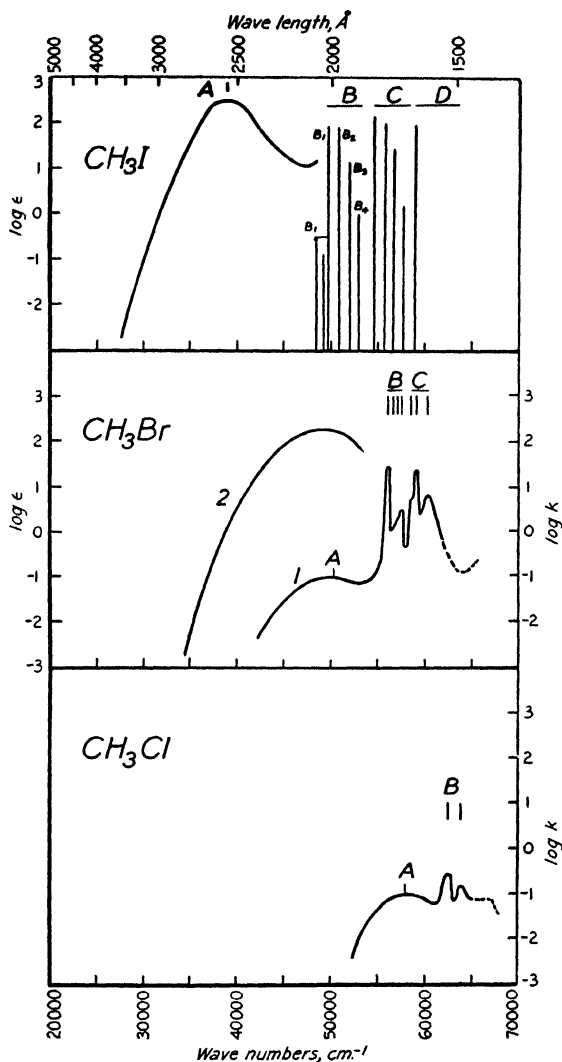


Fig. 36. Extinction Coefficients for the Alkyl Halides. For methyl iodide, the curve is taken from Porret and Goodeve, *Trans. Faraday Soc.*, **33**, 690 (1937), and the lines from Herzberg and Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930). Extinction coefficients, defined by the equation $\epsilon = \frac{1}{cl} \log \frac{I_0}{I}$, apply only to the continuous curve. The values for the lines are approximate. According to Porret and Goodeve, *Proc. Roy. Soc. (London)*, **A166**, 31 (1938), the curve for C_2H_5I is practically the same as that for CH_3I . Two curves are shown for methyl bromide. Curve 1 is qualitative and gives $\log k$ according to Herzberg and Scheibe, *loc. cit.*; k is defined in the same way as is ϵ . Curve 2 is quantitative and gives $\log \epsilon$ according to Porret and Goodeve, *loc. cit.* The curves for C_2H_5Br and C_4H_9Br are practically the same as that for CH_3Br . Only qualitative data (Herzberg and Scheibe) are available for methyl chloride.

TABLE 12

DATA ON ABSORPTION SPECTRA OF SIMPLE ALKYL HALIDES

Substance	Long Wave Beginning of Continuum Å	Maximum of Continuous Absorption Å	Reference
CH ₃ Cl	2200		(1)
	1900	1744	(3)
	1995	1725	(2)
C ₂ H ₅ Cl	2225		(8c)
<i>n</i> C ₃ H ₇ Cl	2230		(8c)
<i>i</i> C ₃ H ₇ Cl	2160		(8c)
<i>n</i> C ₄ H ₉ Cl	2290		(8c)
<i>t</i> C ₄ H ₉ Cl	2215		(8c)
<i>i</i> C ₆ H ₁₁ Cl	2200		(8c)
CH ₂ ClCH ₂ Cl	2240		(8c)
CH ₂ Cl ₂	2500		(4)
	2090		(2)
CH ₃ CHCl ₂	2180		(8c)
CH ₂ ClCHCl ₂	2180		(8c)
CHCl ₂ CHCl ₂	2330		(8c)
CHCl ₃	2600		(4)
	2126		(2)
CCl ₄	2800		(4)
	2280		(2)
C ₂ H ₂ Cl ₂	2370		(8c)
CH ₃ Br	~ 2950	~ 2100	(9)
C ₂ H ₅ Br	~ 2950	~ 2100	(9)
<i>n</i> C ₃ H ₇ Br	2540 (?)		(8c)
<i>i</i> C ₃ H ₇ Br	2520		(8c)
<i>n</i> C ₄ H ₉ Br	~ 2950	~ 2100	(9)
<i>i</i> C ₄ H ₉ Br	2440		(8c)
<i>s</i> C ₄ H ₉ Br	2360		(8c)
<i>t</i> C ₄ H ₉ Br	2660		(8c)
<i>i</i> C ₆ H ₁₁ Br	2260		(8c)
CH ₂ BrCH ₂ Br	2750		(8c)
CH ₂ Br ₂	2507	1689	(2)
CHBr ₃	2863	1695	(2)
CBr ₄	3500		(2)
C ₂ H ₂ Br ₂	2640		(8d)

TABLE 12 (Continued)

DATA ON ABSORPTION SPECTRA OF SIMPLE ALKYL HALIDES

Substance	Long Wave Beginning of Continuum Å	Maximum of Continuous Absorption Å	2nd Maximum Å	3rd Maximum Å	Reference
CH ₃ I	~ 3650	2632			(6)
C ₂ H ₅ I	~ 3650	2632			(9)
nC ₃ H ₇ I		2512	2180		(8)
iC ₃ H ₇ I		2520	2110		(8)
nC ₄ H ₉ I		2512	2205		(8)
iC ₄ H ₉ I		2520	2130		(8)
sC ₄ H ₉ I		2550	2140		(8), (5)
tC ₄ H ₉ I		2611	1859		(7)
iC ₅ H ₁₁ I		2520	2120		(8)
CH ₃ I ₂	3342	3000	1973	1868	(2)
CHI ₃		3490	3070		(10)
CH ₃ Cl ₃		3440	3110		(10)

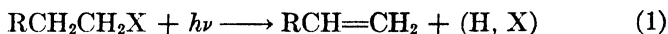
REFERENCES

- (1) Sen-Gupta, *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **2**, 115 (1933).
- (2) Henrieci, *Z. Physik*, **77**, 35 (1932).
- (3) Herzberg and Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930).
- (4) N. K. Saha, *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **2**, 239 (1933).
- (5) Iredale and Mills, *Proc. Roy. Soc. (London)*, **A133**, 430 (1931).
- (6) Porret and Goodeve, *Trans. Faraday Soc.*, **33**, 690 (1937).
- (7) Scheibe, Povenz, and Linstrom, *Z. physik. Chem.*, **B20**, 283 (1933).
- (8a) Hukumoto, *Phys. Rev.*, **42**, 313 (1932). (b) Finkelburg, *Physik. Z.*, **34**, 529 (1933). (c) Hukumoto, *Sci. Rep. Tohoku Univ., Sendai*, **21**, 906 (1932). (d) *ibid.*, **23**, 62 (1934); *Nature*, **134**, 538 (1934).
- (9) Porret and Goodeve, *Proc. Roy. Soc. (London)*, **165**, 31 (1938).
- (10) For solutions in cyclohexane, v. Potterill and Walker, *Trans. Faraday Soc.*, **33**, 363 (1937).

sociation below 1650 Å, and detected two ionization potentials at 9.489 and 10.113 e.v. There has been some discussion as to the nature of the second and third maxima reported (see Table 12) for the iodides. The long wave absorption probably corresponds to dissociation yielding as one product a normal iodine atom. Iredale²⁴ suggested that the second and third maxima correspond to different states of excitation of the iodine atom, whereas Hukumoto²⁰ says that the excess energy in those regions probably goes to the alkyl residues.

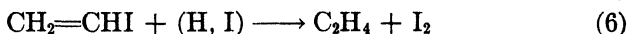
²⁴ Cf. Iredale, *Z. physik. Chem.*, **20**, 340 (1933).

The actual photochemical investigations of these compounds have been confined mainly to the iodides. For the bromides and the chlorides, in the absence of oxygen the quantum yields are in most cases so low as to be practically unmeasurable.²⁵ Even in the case of the iodides, the quantum yields are not high. As for the mechanism of the decomposition, four different primary reactions have been suggested:



Reaction (1) yields a stable alkene and normal or excited hydrogen and iodine atoms, or hydrogen iodide, in the primary act. Of course, an excited halide molecule is formed as an intermediate step in all of these reactions. However, reaction (2) is written as a separate mechanism, in accordance with a suggestion that the excited molecule so formed enters into subsequent reactions with unexcited molecules. Reaction (3) yields, instead of a stable alkene, a stable (but highly reactive) compound containing a divalent carbon atom. Reaction (4), which appears to be the most satisfactory mechanism, is, according to definition (cf. § 4.3), a predissociation process.

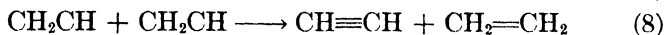
The first mechanism is supported principally by Emschwiller,²⁶ who studied the products of the photolysis and of the photo-oxidation of a number of saturated and unsaturated alkyl halides. For vinyl iodide, for example, he gives the reactions



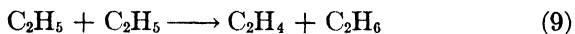
²⁵ In the older literature there are several references to the decomposition of the alkyl halides which are to be discounted because of the probable presence of O_2 or H_2O . The low quantum yields in the decompositions of the pure substances are obviously attributable to rapid back reactions.

²⁶ Emschwiller, *Compt. rend.*, **192**, 799 (1931); *Ann. chim.*, **17**, 413 (1932). Dubrisay and Emschwiller, *Compt. rend.*, **198**, 263 (1934). Emschwiller, *ibid.*, **198**, 464, 1151 (1934); **199**, 854 (1934).

His experiments were conducted in the liquid phase; and this fact, it will be seen later (Chapter XIV), complicates their interpretation. Apparently, Emschwiler discarded the mechanism



because he found an excess of C_2H_2 formed in the reaction. He found, among other interesting results, that under the action of ultraviolet light CH_3I yields CH_2I_2 and CH_4 ; $\text{C}_2\text{H}_5\text{I}$ yields C_2H_4 and C_2H_6 ; propyl and *isopropyl* iodide yield C_3H_6 and C_3H_8 ; and all the butyl iodides, except the tertiary, yield C_4H_8 and C_4H_{10} , whereas the tertiary gives C_3H_6 , C_2H_4 , C_3H_8 , and C_2H_6 . Presumably, in these cases also, reaction (4) is ruled out as the primary step because a lack of stoichiometric equivalence of the products tells against a disproportionation reaction, such as



in the case of ethyl iodide, as a governing step.²⁷

However, the complexity of the reactions involving radicals, which may result in the liquid phase, is such that this lack of correspondence must not be taken as conclusive. Emschwiler has used other evidence based on the oxidation of these compounds, but here again the results are susceptible to a free radical interpretation as well as the one he favors.

Another type of evidence which may be cited for reaction (1) has been obtained by Ramart-Lucas and Salmon-Legagneur.^{27a} They found that liquid *i*-butyl bromide after 48 hours exposure to ultraviolet light was converted to the tertiary compound to the extent of 14 per cent, and reported a similar conversion from *n*-propyl bromide to the *iso* compound. A satisfactory explanation could involve the

²⁷ In the case of ethyl iodide, notably, the yields of C_2H_4 and C_2H_6 are so nearly the same under certain conditions of experiment as to suggest that the discrepancy is due to secondary reactions and that a reaction of the type of (4) may be the true primary step. West and Schlessinger (ref. 32b) suggest a reaction $\text{C}_2\text{H}_5 + \text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_2\text{H}_6 + \text{C}_2\text{H}_4\text{I}$.

^{27a} Ramart-Lucas and Salmon-Legagneur, *Compt. rend.*, **186**, 39 (1928).

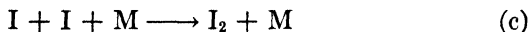
intermediate formation of alkene and hydrogen bromide.^{27b}

The second point of view has been presented by West and Ginsberg,²⁸ who found, as did Emschwiller for methyl iodide, that the quantum yield of photolysis of the vapor of ethyl iodide in the continuum (i.e., $\sim 2600 \text{ \AA}$) is less than 0.01, whereas in the region of band absorption at 2026–1962 $\text{\AA}$ the yield is ~ 0.1 at 30° to 40° over the pressure range of 45 to 90 mm. At pressures of 0.1 mm., the yield is only 0.03. On the other hand, in hexane solutions of concentration equivalent to that of the vapor, the quantum yield in the continuum is 0.6, whereas in the band region the yield in the liquid is about 0.24.

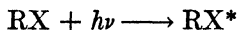
The increase in quantum yield in the vapor on passing from the continuum to the band region may be attributed to the fact that different excitation levels and correspondingly different types of decomposition are involved in the two regions. In the continuum the process is simple rupture:



with a high probability of the reverse reaction, since neither ethyl radicals nor I atoms combine readily to form C_4H_{10} or I_2 . On the other hand, in the liquid the conditions of three-body collisions are always present; once the C_2H_5 and I produced in the primary reaction move out of each other's spheres of influence, there is a good chance for



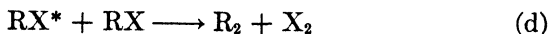
In the discrete region, however, the initial step is excitation to some other hypersurface of relatively high stability (e.g., life of $\sim 10^{-8}$ sec.):



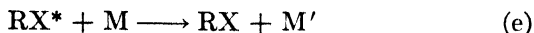
^{27b} An alternative explanation would be that the radical rearranges during the back reaction. The assumption that the radical might rearrange before the back reaction would be contrary to the results obtained by Glazebrook and Pearson on the reactions of the *i*- C_3H_7 radical formed in the photolysis of diisopropyl ketone. See § 8.76 (ref. 114) and § 9.4.

²⁸ W. West and E. Ginsberg, *J. Am. Chem. Soc.*, **56**, 2626 (1934); cf. West and B. Paul, *Trans. Faraday Soc.*, **28**, 688 (1932); cf. also Norton, *J. Am. Chem. Soc.*, **56**, 2294 (1934).

The resultant molecules have a slight chance to react with other molecules:



or to be deactivated in collisions:



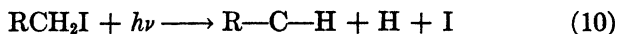
or even to decompose in a slow spontaneous process:



which, because of subsequent recombination, actually reduces the yield in the vapor phase. Nevertheless, because of reaction (d), the quantum yield in the discrete region is greater than in the continuum—but only in the vapor phase.

Most of the net decomposition which occurs in the vapor phase is accounted for by reaction (d). Only a relatively small amount of the product is obtained via reaction (f), because of the high efficiency of the back reaction. In the liquid phase, that portion of the molecules which decomposes via reaction (f) is not increased; but, since the back reaction of the product radicals is decreased, there is an increase in the net yield of that reaction. The conditions in solution favor reaction (e) at the expense of (d); hence, although the quantum yield increases, the effect is not so great as in the continuum. The quantum yield of 0.24 in the band region as compared to 0.6 in the continuum suggests that in solution ~ 40 per cent of the molecules absorbing in the band region decompose via reaction (f).

Parti and Samuel,²⁹ reasoning primarily from valence and energy considerations, arrive at conclusions favoring the primary reaction (3). According to the pair-bond theory of valence,^{29a} the unexcited carbon atom can only be bivalent. They suggest that, for the iodides, the primary step is always



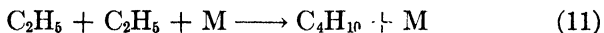
where only an unexcited RCH and H are produced, but where the I atom may be either in a $^2P_{3/2}$ or a $^2P_{1/2}$ state.

²⁹ Parti and R. Samuel, *Current Sci.*, **5**, 386 (1937).

^{29a} Cf. Van Vleck and A. Sherman, *Rev. Mod. Phys.*, **7**, 167 (1935).

According to Parti and Samuel, the beginnings of the first selective absorptions for twelve alkyl halides agree with estimates as to the differences of the energy contents of molecules containing tetravalent and divalent carbons. Furthermore, certain energy differences in the absorption spectra are said to correspond to the energy difference ${}^2P_{3/2} - {}^2P_{1/2}$ for the iodine atom.

On the other hand, the results of Bates and Spence³⁰ on the photodecomposition and photo-oxidation of methyl and ethyl iodides are well interpreted on the assumption that the primary step is the decomposition into free alkyl plus an iodine atom, as in reaction (4). In the prolonged photodecomposition of ethyl iodide vapor, Jones and Bates³¹ obtained a very small yield of gas uncondensable at solid carbon dioxide-ether temperatures, which they concluded (without analysis) to be ethylene and ethane and attributed to the disproportionation reaction (9) between the ethyl radicals formed in the primary step. It is interesting to note that, if the mechanism involving reactions (4) and (9) is correct, the results of the studies on ethyl iodide indicate very definitely that at ordinary temperatures the reaction



is extremely slow in comparison with the disproportionation reaction (9).

The most direct evidence as to the nature of the primary step in the vapor state is that of West,^{32a} who detected free radicals in the photolysis of methyl iodide by the use of the para-ortho hydrogen conversion method (cf. § 5.6). Unfortunately, the conversion is also susceptible to the presence of free atoms; hence all that may be concluded from West's results is that either free radicals or free atoms, or both, are produced. Since the presence of free atoms is

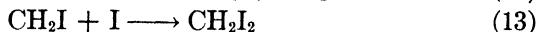
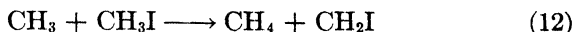
³⁰ Bates and Spence, *J. Am. Chem. Soc.*, **53**, 1689 (1931); *Trans. Faraday Soc.*, **27**, 414 (1931).

³¹ Jones and Bates, *ibid.*, **56**, 2285 (1934).

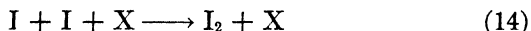
³² (a) West, *ibid.*, **57**, 1931 (1935). (b) West and Schlessinger, *ibid.*, **60**, 961 (1938). (c) Cf. also Iredale and Stephan, *Trans. Faraday Soc.*, **33**, 800 (1937), who studied the photolysis of CH_3I and HI in the vapor state.

assumed in all mechanisms, this particular result offers no basis for choice between them.

West and Schlessinger^{32b} have attempted to solve the difficulty by a study of the photolysis of various alkyl iodides in the presence of silver. In this way iodine atoms formed in the primary step were rapidly removed, thus cutting down recombination and increasing the quantum yields. They presented evidence in the case of methyl iodide for the reactions



which would account for the products noted by Emschwiller. Photolysis of the CH_2I_2 may produce C_2H_4 . According to West and Schlessinger, the quantum yield of photolysis of alkyl iodides is increased by any means which may interfere with recombination; e.g., the removal of iodine atoms to form I_2 molecules. The reaction



is favored by addition of foreign gas. Increase of CO_2 pressure from 10 to 40 atmospheres increases the relative yield of photolysis of ethyl iodide from 0.049 to 0.135, as compared with 1.0 in hexane solution. The weight of evidence seems to be in favor of the free radical mechanism.

Diiodides have also been studied. For the photolysis of ethylene iodide in CCl_4 solution by light of $< 3600 \text{ \AA}$ at room temperature, DeRight and Wiig³³ report a quantum yield of ~ 0.75 . Forbes and Nelson³⁴ state that the quantum yield of the photolysis of butylene iodide in solution at -55° and $\sim 2537 \text{ \AA}$ is ~ 0.7 , rising to ~ 1.0 at -20° and to ~ 1.1 at 25° .³⁵

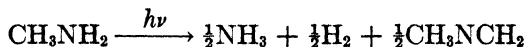
³³ DeRight and Wiig, *J. Am. Chem. Soc.*, **57**, 2411 (1935); cf. *ibid.*, **58**, 693 (1936).

³⁴ Forbes and Nelson, *ibid.*, **59**, 693 (1937).

³⁵ Further data on the photochemistry of the iodides are included in the chapter on the liquid state (see § 14.23). In respect to the chlorides, Hill, *J. Am. Chem. Soc.*, **54**, 32 (1932), reports a quantum yield of 4 moles of HCl (but no Cl_2) in the photolysis of chloroform studied by a streaming method. Mahneke and Noyes, *ibid.*, **58**, 932 (1936), report some inconclusive experiments on the photochemistry of *cis*- and *trans*-dichloroethylenes at 1980–1860 $\text{\AA}$.

8.3 Amines. The amines show a characteristic band absorption in the range 2500–2100 Å.³⁶ The bands, like those of ammonia (cf. § 7.7), are broad and diffuse, and increase in intensity toward the ultraviolet. Since the absorption intensity is of the same order of magnitude for the different primary amines, it is concluded that an electron jump in the NH₂ group is involved. Similar results are obtained with (CH₃)₂NH, (CH₃)₃N, and (C₂H₅)₂NH, the bands becoming so diffuse as to give the appearance of a continuum. C₆H₅NH₂ shows 220 bands in the range 2980–2632 Å. The absorption at 2800 Å may be attributed to an electron jump in the benzene kernel (cf. § 8.14). A second and much stronger (almost continuous) absorption setting in rather sharply at 2430 Å is not shown by benzene itself. The ultraviolet absorption spectrum of pyridine, C₅H₅N,³⁷ may be compared with that of phenylamine. It consists of 300 discrete bands between 3100 and 2500 Å. Beyond 2750 Å the bands become diffuse. Decomposition takes place below that wave length.

Very little attention has been given to the photochemistry of the amines. For CH₃NH₂ and C₂H₅NH₂, it is known only that the photolysis yields hydrogen, methane, ethane, and nitrogen, together with a small amount of liquid (containing nitrogen) of uncertain composition.^{38a} As in the case of the alkyl halides (cf. § 8.2), the quantum yield is extremely low at room temperatures. According to Emeleus and Jolley,^{38b} the quantum yield of the reaction



is 0.7 at 100° to 105°.

The photo-oxidation has also been investigated in an at-

³⁶ Herzberg and Kolsch, *Z. Elektrochem.*, **39**, 572 (1933). For the deuterio-amines, see Förster and Jungers, *Physik. Z.*, **38**, 140 (1937). For phenylamine, cf. Savard, *Bull. soc. chim.*, **53**, 1404 (1933). Banov and Prilezajewa, *Compt. rend. (Leningrad)*, **3**, 498 (1934), have observed fluorescence in C₂H₅NH₂ between 3500 and 2700 Å.

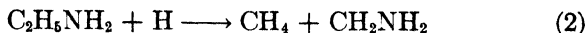
³⁷ Henri and Angenot, *J. chim. phys.*, **33**, 641 (1936).

³⁸ (a) H. E. Emeleus and H. S. Taylor, *J. Am. Chem. Soc.*, **53**, 3370 (1931); (b) Emeleus and Jolley, *J. Chem. Soc.*, 1612 (1935).

tempt to elucidate the photolysis. However, at the present time there is no certainty as to the nature of the primary step. The presence of CH_4 among the products of the photolysis of $\text{C}_2\text{H}_5\text{NH}_2$ indicates the probability that the primary step involves, not the formation of free C_2H_5 radicals, but rather the splitting off of a hydrogen atom from the amine group:



followed by

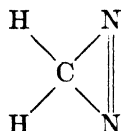


From analogy to the reaction between D and C_2H_6 (cf. Table 33, Appendix III), the latter reactions appear to have an energy of activation of ~ 7.5 kcal. There is another possibility, of course, involving the formation of free methyl radicals in the primary step



the latter reacting with some other molecule to yield CH_4 .

8.31 Diazomethane. The absorption spectrum of diazomethane consists of a diffuse band region followed by a continuum in the range 4710–3200 Å, and of a continuum beginning at 2650 Å and extending toward shorter wave lengths.³⁹ The qualitative course of the extinction coefficient is shown in Fig. 37 (p. 214). The diffuseness in the longer wave length region is indicative of predissociation. Kirkbride and Norrish have interpreted the close resemblance between the spectra of CH_2N_2 and of azomethane (cf. § 8.32) as indicating the structure



whereas Rice and Rice⁴⁰ use the formula $\text{H}_2\text{C}=\text{N}\equiv\text{N}$.⁴¹

³⁹ Kirkbride and Norrish, *J. Chem. Soc.*, 119 (1933).

⁴⁰ F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals*, Johns Hopkins Press, Baltimore, 1935.

⁴¹ Cf. Harrold, Hemphill, and Ray, *J. Am. Chem. Soc.*, **58**, 747 (1936).

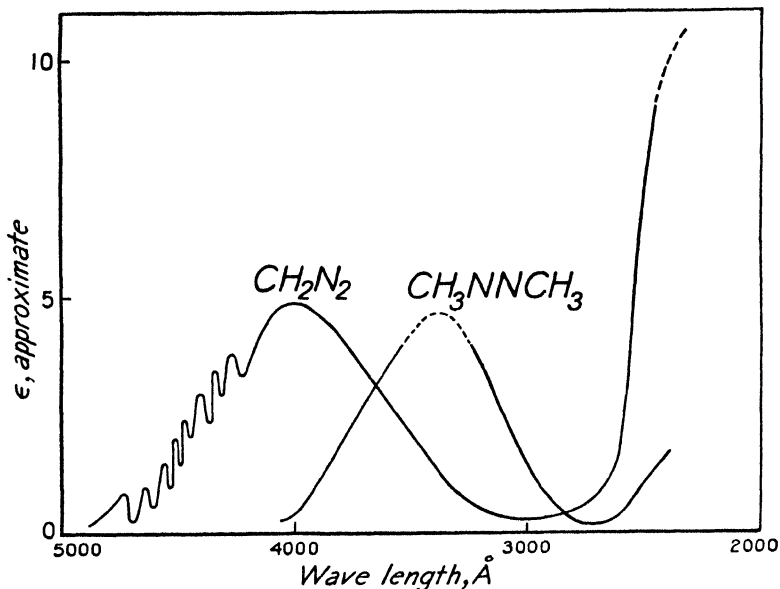
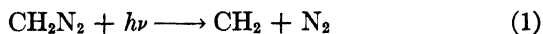


Fig. 37. Absorption Curves for Diazomethane and Azomethane, according to Kirkbride and Norrish, *J. Chem. Soc.*, 119 (1933), and Ramsperger, *J. Am. Chem. Soc.*, **50**, 123 (1928), respectively.

The quantum efficiency of the photodecomposition is ~ 4 at both 4360 and 3650 Å. The products are mainly nitrogen, ethylene, propylene, and a non-volatile liquid which is possibly a pyrazoline derivative. From these facts and from the photochemical behavior of mixtures of diazomethane with hydrogen and with oxygen, Kirkbride and Norrish have concluded that the primary process in the photochemical decomposition is

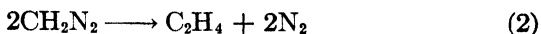


Subsequent steps involving the action of CH_2 radicals or excited ethylene molecules probably explain the products formed.

This mechanism is to be contrasted with that suggested by Steacie⁴² for the thermal decomposition. He found a homogeneous bimolecular reaction to proceed at tempera-

⁴² Steacie, *J. Phys. Chem.*, **35**, 1493 (1931).

tures above 135°, with a heat of activation of 36 kcal. per mole, according to the equation



The results of Rice and Glasebrook,⁴³ who employed the mirror method of detecting free radicals (§ 5.91), suggest that, in the thermal decomposition also, the reaction proceeds through the intermediary of free radicals.⁴⁴

8.32 Azomethane. The absorption spectrum of azomethane, as shown in Fig. 37,⁴⁵ consists of two regions very similar to those of diazomethane, except that in this case both the region 4060–2800 Å and that beginning at ~ 2600 Å appear to be continuous. This appearance of continuity (cf. § 4.34) is by itself no indication of the process involved in the case of large molecules. Judging from the resemblance to diazomethane (§ 8.31), it is possible that in this case also the first region is indicative of a predissociation process.

Azomethane has been intensively studied by a number of investigators because it was apparently an example of a compound which, in the thermal process, decomposed unimolecularly without chain or complicating side reactions. There has been some disagreement as to the quantum efficiency of the photolysis.

According to Ramsperger,⁴⁶ two $\text{CH}_3\text{N}=\text{NCH}_3$ molecules are decomposed per quantum absorbed, whereas more recent and extensive investigations of Forbes, Heidt, and Sickman⁴⁷ indicate that the quantum efficiency of the reaction is only 1.0 and is unaffected by temperature up to 226°. Unfortunately, these conclusions were based on a study of the pressure change during the photolysis and on

⁴³ Rice and Glasebrook, *J. Am. Chem. Soc.*, **55**, 4329 (1933); **56**, 2381 (1934).

⁴⁴ Cf. Rice and Glasebrook, *ibid.*, **56**, 741 (1934), for similar experiments with diazoethane. From these experiments it was concluded that the free ethylidene (CH_3CH) radicals formed in the primary step are extremely unstable and immediately rearrange to form ethylene.

⁴⁵ Ramsperger, *J. Am. Chem. Soc.*, **50**, 123 (1928).

⁴⁶ Ramsperger, *ibid.*, **49**, 912, 1435 (1927).

⁴⁷ Forbes, Heidt, and Sickman, *ibid.*, **57**, 1935 (1935).

the assumption that the decomposition might be represented largely by the overall reaction



Subsequent studies by Burton, Davis, and Taylor ⁴⁸ indicate that this is far from true, and that variable amounts of nitrogen, methane, ethane, and propane, as well as unsaturated hydrocarbons (depending upon the degree of decomposition as well as the temperature), are formed. As the result of experiments in which they used nitric oxide as a detector of free radicals (cf. § 5.91), Davis, Jahn, and Burton ⁴⁹ concluded that the primary step of the photolysis is



and that reaction (1) does not occur to any appreciable extent. However, the possibility of the reaction



as an intermediate stage was not eliminated. The CH_4 and C_2H_6 , as well as other compounds formed in the photolysis, are attributed to reactions between free CH_3 radicals, formed in reaction (2), and other molecules, such as those of azomethane. The ethane is not formed by the direct combination of methyl radicals.

8.4 Nitro-alkanes and the alkyl nitrites and nitrates.

The qualitative course of the absorption spectra of some of these compounds ⁵⁰ is shown in Fig. 38 (p. 218). The nitrites show broad band absorption in the region 4000–3100 Å; the spectra of ethyl and amyl nitrites are practically identical.⁵¹ No fluorescence is reported.

The products of photolysis of the nitrites include nitrogen, nitrous oxide, and carbon monoxide in all cases. In addition,

⁴⁸ Burton, Davis, and Taylor, *ibid.*, **59**, 1038, 1989 (1937); cf. Heidt and Forbes, *ibid.*, **57**, 2331 (1935).

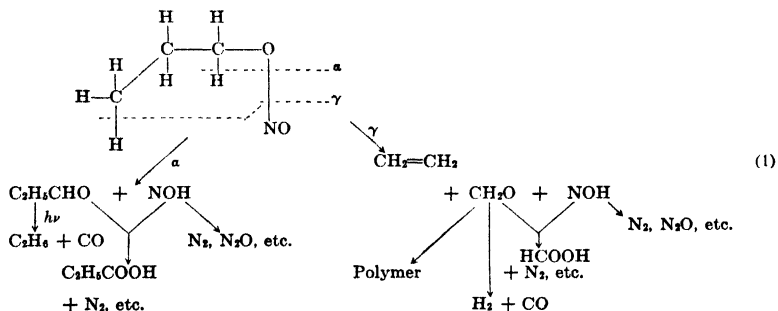
⁴⁹ Davis, Jahn, and Burton, *ibid.*, **60**, 10 (1938).

⁵⁰ (a) Thompson and Purkis, *Trans. Faraday Soc.*, **32**, 674 (1936). Cf. (b) Goodeve, *ibid.*, **30**, 504 (1934); (c) Hirschlauff and Norrish, *J. Chem. Soc.*, 1580 (1936); (d) Thompson and Dainton, *Trans. Faraday Soc.*, **33**, 1546 (1937).

⁵¹ A number of other alkyl nitrites have been examined by Thompson and Dainton (ref. 50d); their spectra are similar to those described here.

methyl nitrite yields formaldehyde and a trace of hydrogen; the others yield various alkanes, aldehydes, ketones, and acids.^{50d, 52} According to Thompson and Dainton^{50d} all the photochemical data may be interpreted by supposing that an NOH radical is split off, together with either an aldehyde or ketone or unsaturated hydrocarbon or more than one of these. The H in the NOH radical may come from one of the carbon atoms α , β , or γ to the nitrite group. This simultaneous splitting of the molecule in more than one place is one type of predissociation process and is in conformity with the diffuse band structure of the absorption spectrum.

The scheme for the photolysis of *n*-propyl nitrite, for example, is given as follows:⁵³



The mechanism proposed for the primary step is in close agreement with that suggested for the case of the photolysis of some complicated nitroso compounds in solution;⁵⁴ it is to be contrasted with that suggested by Steacie and his co-workers⁵⁵ for the primary step of the pyrolysis; namely,



Hirschlaff and Norrish^{50c} have examined the products of photolysis of nitromethane and nitroethane when illuminated by light of 3000–2000 Å. N₂, CO, NO, and CO₂, as well as unanalyzed residue, were found among the product

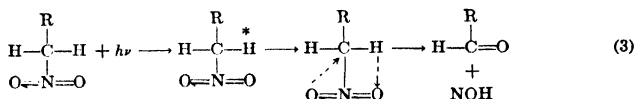
⁵² Purkis and Thompson, *Trans. Faraday Soc.*, **32**, 1466 (1936).

⁵³ For the photochemistry of the aldehyde products, see § 8.72.

⁵⁴ Anderson, Crumpler, and Hammick, *J. Chem. Soc.*, 1679 (1935).

⁵⁵ Cf. Steacie and Shaw, *Proc. Roy. Soc. (London)*, **A146**, 388 (1934).

gases in both cases. In addition, NO_2 and unsaturated hydrocarbons were found in the case of nitroethane. The products of the decomposition are represented quantitatively as resulting from a series of changes:



This is a good illustration of a stable constellation of atoms in a molecule rearranging, when excited, to give two other constellations as products.

The final products are explained by secondary reactions of decomposition and oxidation by the oximino radicals.

No photochemical studies of the nitrates are reported. Their well-known explosive nature⁵⁶ has perhaps discouraged such investigations.

8.5 Alcohols. Both methyl and ethyl alcohols are transparent in the near ultraviolet. At 2000 Å, as may be seen in Fig. 39,⁵⁷ a continuum sets in.⁵⁸ Evidence of some diffuse structure is indicated in photographs taken by Price.⁵⁹ No fine structure has been reported.

The continuum does not appear to correspond to a

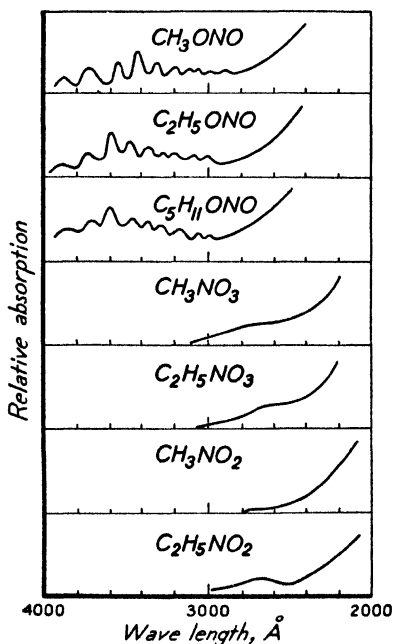


Fig. 38. Absorption Curves for Some Alkyl Nitrites, Alkyl Nitrates, and Nitroalkanes, according to Thompson and Purkis, *Trans. Faraday Soc.*, **32**, 674 (1936).

⁵⁶ Cf. Jahn, *J. Am. Chem. Soc.*, **59**, 1761 (1937).

⁵⁷ The spectrum of ethanol is similar to that of methanol.

⁵⁸ Herzberg and Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930).

⁵⁹ Price, *J. Chem. Phys.*, **3**, 256 (1935).

dissociation into alkyl and hydroxyl. According to Patat,⁶⁰ who used the para-ortho hydrogen conversion method of testing, no hydrogen atoms are formed in the photolysis. Since this method is sensitive to free radicals in general (*v.*

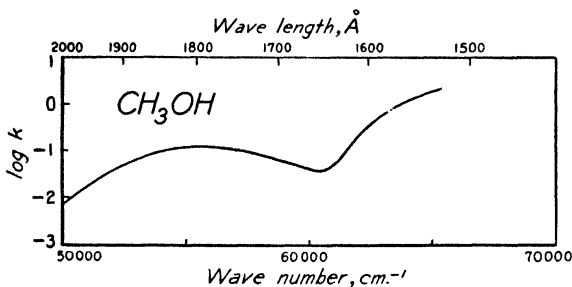


Fig. 39. Qualitative Course of the Extinction Coefficient for Methanol, according to Herzberg and Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930). Here k is defined in arbitrary units.

§ 5.91), any decomposition in which free radicals may be assumed to be formed is ruled out.⁶¹ The products of the photolysis include hydrogen, carbon monoxide, and aldehyde. The primary step is probably



the RCHO undergoing further photolysis as described in § 8.72. The quantum yield of the primary step is of the order of unity. According to Price,⁵⁹ the excitation is in the C—O bond, a statement directly contradictory to that made by Patat and Hoch⁶⁰ at about the same time. Although this point may be controversial, this is quite probably a case of an excited constellation of atoms rearranging, in the excited state, to form two other stable constellations, which then fly apart from each other in much the same manner as the “separating half” of a collision.

Fletcher⁶² has found it necessary to postulate a similar

⁶⁰ Patat, *Anz. Akad. Wiss. Wien, Math.-naturw. Klasse*, **1933**, 93; Patat and Hoch, *Z. Elektrochem.*, **41**, 434 (1935).

⁶¹ This statement assumes the validity of the method. The para-ortho conversion has been known to fail as a method of testing for free H atoms (cf. § 5.91).

⁶² Fletcher, *Proc. Roy. Soc. (London)*, **A147**, 119 (1934).

mechanism for the pyrolysis of methanol. He found that the energy of activation of the first step is 68 kcal.; i.e., much less than the 142.1 kcal., corresponding to the 2000 Å at which the continuum begins. Evidently, the photochemical excitation of the molecule requires much more energy than that necessary for the actual dissociation.

Terenin and Neujmin⁶³ report that they detected free hydroxyl radical by its emission spectrum in the photolysis of CH₃OH in the Schumann region. However, such small amounts of OH are detectable by emission⁶⁴ that it is reasonable to conclude, in view of the findings of Patat, that they are insignificant in this case (cf. formic acid, § 8.8) and that, particularly at longer wave lengths, reaction (1) is the correct primary step.⁶⁵ The wave length 1560 Å, below which it was necessary to go to observe the OH emission band, corresponds to 182 kcal. per mole. Allowing 92 kcal. (corresponding to the emission band) for the energy of activation of the OH radical, it follows that 90 kcal. is an upper limit for the strength of the C—O bond in alcohols.

The photolyses of aqueous solutions of the alcohols in the full light of the mercury arc have also been investigated by L. Farkas and Hirshberg,^{65a} who showed that below 2000 Å decomposition takes place according to reaction (1) for methyl, ethyl, and propyl alcohols. *Iso*-propyl alcohol, as might be expected, yields H₂ and acetone. The aldehyde or ketone formed in the photolysis of these alcohols is also decomposed photochemically (cf. §§ 8.72, 8.76), but it is interesting to note that such an effect is less in the case of CH₃OH, where HCHO is the product. The explanation is that, whereas the other aldehydes are sensitive to light below 2900 Å in aqueous solution, formaldehyde in such solution is sensitive only below 2350 Å (cf. § 8.7). The

⁶³ Terenin and Neujmin, *Nature*, **134**, 255 (1934); *J. Chem. Phys.*, **3**, 436 (1935).

⁶⁴ Cf. Oldenberg, *J. Chem. Phys.*, **3**, 266 (1935); Burton, *J. Am. Chem. Soc.*, **58**, 1655 (1936); Henkin and Burton, *ibid.*, **60**, 831 (1938).

⁶⁵ The photo-oxidation of the alcohols may perhaps involve reaction (1) as the primary step, as evidenced by the formation of aldehydes and acids among the products. Cf. Cantieni, *Ber.*, **69B**, 1101, 1386 (1936).

^{65a} L. Farkas and Hirshberg, *J. Am. Chem. Soc.*, **59**, 2450 (1937).

quantum yield for the decomposition of $\text{C}_2\text{H}_5\text{OH}$ was found to be only 0.8, indicating some deactivation by the solvent. By the use of solutions in heavy water and examination of the isotopic composition of the products, it was shown that one H atom came from the R group and one from the OH in the alcohol.

8.6 Alkyl cyanides. The qualitative course of the extinction coefficient of methyl cyanide is given in Fig. 40.⁵⁸ The continuum in this case begins at 1910 Å. When CH_3CN is decomposed by light of 1600 Å, the emission bands of

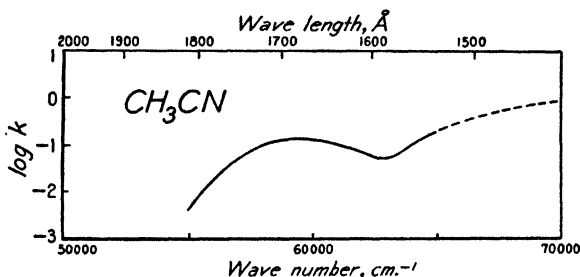


Fig. 40. Qualitative Course of the Extinction Coefficient for Methyl Cyanide, according to Herzberg and Scheibe, *Z. physik. Chem.*, **B7**, 390 (1930). Here k is defined as for Fig. 39, p. 219.

the excited CN radical are observed.⁶³ However, this is such a sensitive method of detection (cf. the alcohols, § 8.5, and formic acid, § 8.8) that it cannot be said with certainty that the primary step of the photolysis at longer wave lengths is the decomposition into free radicals by rupture of the C—C bond. The wave length 1600 Å corresponds to 178 kcal. per mole. From the energy of excitation of the CN radical (73 kcal.), Terenin and Neujmin obtain an upper limit of 105 kcal. for the strength of the C—C bond in this case.

8.7 General aspects of absorption spectra of aldehydes and ketones. The aldehydes, as well as the ketones, are characterized by the existence of two absorption regions, the first of which begins at $\sim 3500\text{--}3300$ Å and has a maximum at $\sim 2900\text{--}2800$ Å, and the second of which begins

at 2400 Å or less. There is considerable difference in such details as diffuseness, but the overall resemblance may be seen clearly in a diagram such as Fig. 41, which gives the molecular extinction coefficients of several aldehydes in hexane solution ⁶⁶ (one of the effects of solution being to

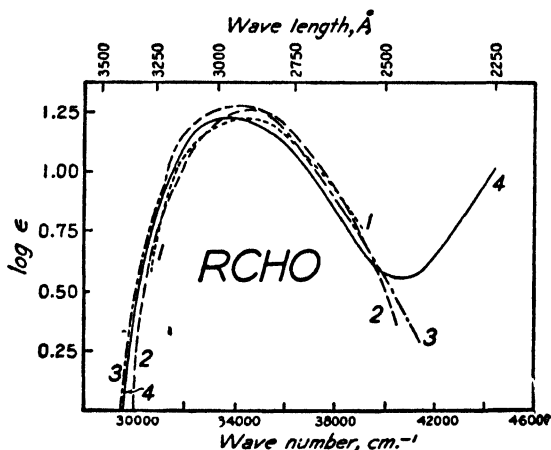
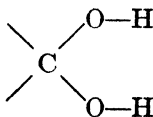


Fig. 41. Molecular Extinction Coefficients of Aldehydes in Hexane Solution, according to Wolf and Herold, *Z. physik. Chem.*, **B12**, 165 (1931).

$\epsilon = \frac{1}{cd} \log \frac{I_0}{I}$. (1) Acetaldehyde. (2) Propionaldehyde. (3) *n*-Butyraldehyde. (4) *i*-Butyraldehyde in heptane. Cf. Levene and Rothen, *J. Chem. Phys.*, **4**, 48 (1936).

erase the evidence of structure). However, it is seen that in general the principal band appears with a maximum at about 2800–2900 Å in those cases in which the solvent does not react with the carbonyl group. When a solvent reacts with the carbonyl group; e.g., water to give



the absorption maximum may be considerably displaced

⁶⁶ (a) Herold and Wolf, *Z. physik. Chem.*, **B12**, 165 (1931). (b) Cf. Conrad-Billroth, *ibid.*, **B23**, 315 (1933). (c) Snow and Eastwood, *Nature*, **133**, 908 (1934).

toward the ultraviolet. A similar effect results from acetate formation.^{66a, 67}

The facts just cited are generally accepted as a basis for the conclusion that the excitation takes place in the carbonyl group. If the statement is correct, it follows that the molecular extinction coefficients of the different aldehydes and ketones should be nearly the same at any particular wave length. That this is so may be seen from Figs. 41 and 42, from which the values for four aldehydes and acetone may be read. If excitation took place in any one of the C—H linkages, the molecular extinction would increase with the size of the molecule. If it took place only at C—H linkages on the C atom α to the C=O group, the coefficient would be greater for acetone and less for isobutyraldehyde. If it

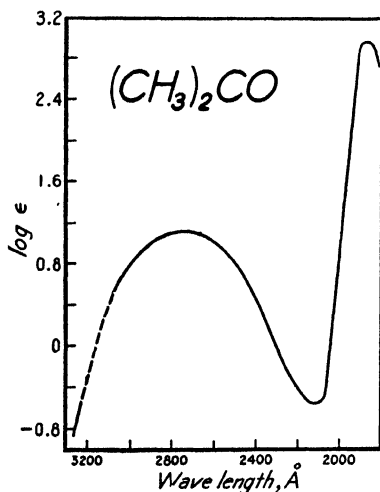


Fig. 42. Extinction Coefficient of Acetone in Hexane Solution, according to Ley and Arends, *Z. physik. Chem.*,

B12, 132 (1931). $\epsilon = \frac{1}{cl} \log \frac{I_0}{I}$.

took place only at the C—CO linkage, the coefficient would be twice as great for acetone as for the aldehydes. Thus the great similarity of the curves of the molecular extinction coefficients in the first absorption region indicates that the absorption takes place by excitation of an electron in the carbonyl group.

Henri and Wurmser⁶⁸ showed that it was absorption in this region of the spectrum which is responsible for the photolysis of the aldehydes and ketones

observed by Berthelot and Gaudechon.⁶⁹

⁶⁷ Cf. Wolf and Herold, *Z. physik. Chem.*, **B5**, 124 (1929); Henri and Schou, *Z. Physik*, **49**, 774 (1928); Ramart-Lucas and Guerlain, *Bull. soc. chim.*, **49**, 1860 (1931). The shift in aqueous solutions of HCHO is particularly marked; the absorption then begins at ~ 2350 Å.

⁶⁸ Henri and Wurmser, *Compt. rend.*, **156**, 230 (1913).

⁶⁹ Berthelot and Gaudechon, *ibid.*, **151**, 478 (1910); et seq.

8.71 Special aspects of absorption spectra of the aldehydes. Reference to Table 13 indicates that, while in a general way the absorption spectra of the aldehydes resemble each other, there are some marked points of difference. In particular, it should be noted that the first absorption range of formaldehyde is divided into three distinct regions, where the spectrum is successively discrete, diffuse, and continuous; whereas, in the case of all the others (except benzaldehyde),

TABLE 13

NEAR-ULTRAVIOLET ABSORPTION SPECTRA OF THE VAPORS OF THE ALDEHYDES

Substance	SPECTRUM RANGE, Å			Fluorescence Caused by	Reference
	Discrete	Diffuse	Continuous		
HCHO	3570-2750	2750-2500	< 2670	3530, 3400, 3270	(1), (2a), (3-6)
CH ₃ CHO	3484-3050	3050-2660	3484-~2400	3342-2804	(1), (7-10), (12), (17)
C ₆ H ₅ CHO		3400-2700	3400-~2400		(11), (12)
n-C ₇ H ₇ CHO		3400-2700	3400-2350	3130	(13)
i-C ₇ H ₇ CHO		3400-2700	3400-2350		(13)
Acrolein					
CH ₂ =CHCHO	4000-3300	3300-2800	4000-2400		(14-16)
Crotonaldehyde					
CH ₃ CH=CHCHO	3850-3350	3350-2900	4000-2600		(12), (15)
C ₆ H ₅ CHO	3747-2599	2428-2349			(2b)

REFERENCES

- (1) V. Henri and S. A. Schou, *Z. Physik*, **49**, 774 (1928).
- (2) V. Henri, *The Structure of Molecules*, P. Debye, Editor, Blackie and Son, Ltd., London, 1932: (a) p. 126; (b) p. 124.
- (3) Herzberg, *Trans. Faraday Soc.*, **27**, 378 (1931).
- (4) Dieke and Kistiakowsky, *Proc. Nat. Acad. Sci.*, **18**, 346 (1932); *Phys. Rev.*, **45**, 4 (1934).
- (5) Price, *J. Chem. Phys.*, **3**, 256 (1935).
- (6) Herzberg and Franz, *Z. Physik*, **76**, 720 (1932); S. Gradstein, *Z. physik. Chem.*, **B22**, 384 (1933).
- (7) J. H. C. Smith, *Carnegie Inst. Wash. Publ.*, **27**, 178 (1928).
- (8) Schou, *Doctorate Thesis*, Les Presses Universitaires de France, Paris, 1928.
- (9) Henri, *Trans. Faraday Soc.*, **25**, 765 (1929).
- (10) P. A. Leighton and Blacet, *J. Am. Chem. Soc.*, **55**, 1766 (1933).
- (11) Leighton and Blacet, *J. Am. Chem. Soc.*, **54**, 3165 (1932).
- (12) Leighton, *Chem. Rev.*, **17**, 393 (1935).
- (13) Leighton, Levanas, Blacet, and Rowe, *J. Am. Chem. Soc.*, **59**, 1845 (1937).
- (14) Thompson and Linnett, *J. Chem. Soc.*, 1425 (1935).
- (15) Blacet, Young, and Roof, *J. Am. Chem. Soc.*, **59**, 608 (1937).
- (16) Blacet, Fielding, and Roof, *J. Am. Chem. Soc.*, **59**, 2375 (1937).
- (17) Schou, *J. chim. phys.*, **27**, 27 (1929).

the continuum appears as a background throughout the whole range. It will be seen (§ 8.72) that the differences in the spectra are reflected by differences in the chemical processes involved.⁷⁰

The reader should be cautious in the use of Table 13. The limits given to the various regions are sometimes based on the judgment of the investigators concerned and sometimes on our own. The regions indicated do exist; the limits given are subject to correction. For a better understanding of the following sections, the existence of these regions and their rough limits should be borne in mind.

8.72 Photochemistry of the aliphatic aldehydes. The aldehydes are distinguished by the fact that, although absorption of energy occurs exclusively in the C=O bond, rupture of that bond is not involved in the photolysis.⁷¹ Consequently, decomposition always occurs through a predissociation process of one of the types previously discussed. It is impossible to write a simple net reaction for the photolysis of these compounds. Although, with the exception of formaldehyde, mixtures of alkanes and CO are generally produced, there is also evidence for polymerization as well as H₂ formation; in the higher aldehydes, lower aldehydes and alkenes may also be among the products. The various photoreactions into which an aldehyde molecule can enter may be summarized as follows.

Simple activation

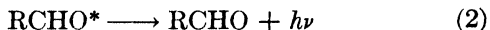


of necessity, precedes all the other reactions and occurs in all regions of the spectrum. A fine-line spectrum, such as that shown by formaldehyde down to 2750 Å, indicates a long lifetime of the excited state; a pure continuum, such as that reported for propionaldehyde, may be due in part to close-packed rotation structure and in part to the short lifetime of the excited state. Different processes, it must

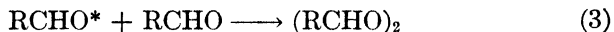
⁷⁰ For a more thorough discussion of this subject, see Burton and Rollefson, *J. Chem. Phys.*, **6**, 416 (1938). Cf. §§ 4.2 et seq.

⁷¹ See the discussion of reaction (7) later in this section (p. 229).

be emphasized, can occur for different individual molecules in one reaction system. The energy absorbed may be employed in various ways. It may be dissipated by *fluorescence*:



by *polymerization*:



by *collisional deactivation*:

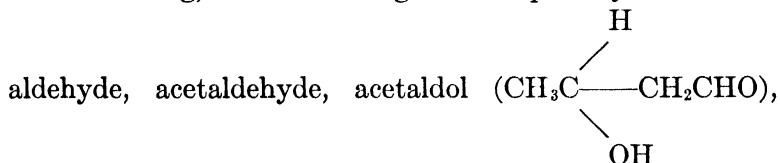


where M may be a second RCHO molecule and the energy is distributed between the two molecules after the collision; or perhaps by decomposition induced by an external field of force; i.e., *induced predissociation*:

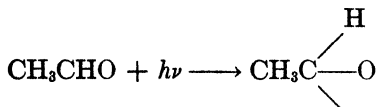


as well as by other predissociation reactions, which are considered later in this section.

Polymerization, as in reaction (3), has been found to take place for all the aldehydes, when the experiments are conducted at room temperature. In this connection, an interesting group of studies has been carried out by Farkas and Hirshberg,^{71a} who investigated the photolysis of form-



crotonaldehyde, and propionaldehyde in aqueous solutions in the full light of a mercury arc. The quantum yields are modified in an uneven way by the solvent, being ~ 0.3 for HCHO , 1.3 for CH_3CHO , 0.9 for $\text{C}_2\text{H}_5\text{CHO}$, and 0.5 for crotonaldehyde. CH_3CHO yields mainly acetaldol, indicating (according to Hirshberg and Farkas) that the primary step is



^{71a} Hirshberg and L. Farkas, *J. Am. Chem. Soc.*, **59**, 2453 (1937). Cf. R. N. Smith, Leighton, and Leighton, *ibid.*, **61**, 2299 (1939).

which thereafter reacts with a second molecule to yield the aldol. Some acid is formed in the photolysis of C_2H_5CHO and $HCHO$.

That reactions (1), (2), and (4) occur generally is evidenced in two ways: by the facts that, in the case of all the aldehydes, the quantum yield in the discrete portion of the spectrum is generally lower than at the shorter wave lengths,⁷² and that fluorescence has been directly observed in many cases. As for reaction (5) it has been suggested⁷³ that it occurs in the fine-structure region of formaldehyde. Evidence against such an assumption is presented below in connection with the discussion of reaction (8).⁷⁴

Decomposition into free radicals



seems to occur in all cases. For formaldehyde, the mechanism is supported by work of Patat⁷⁵ on the influence of added oxygen on the hydrogen yield, as well as by the work of Akeroyd and Norrish⁷⁶ on the quantum yield of photolysis at elevated temperatures. Such evidence for the production of free hydrogen atoms in the photolysis of formaldehyde is indirect; it seems that, if present, they ought to be detectable by the mirror method (cf. § 5.91). That method has been used successfully by Pearson and Purcell,⁷⁷ who detected free methyl radicals in the photolysis of acetaldehyde. The evidence for reaction (6) in the case of the other

⁷² See the series of papers by Leighton and Blacet and their co-workers, indicated in Table 13. Unless otherwise stated, most of the conclusions of this section are based on work reported in those investigations.

⁷³ Cf. Norrish and Kirkbride, *J. Chem. Soc.*, 1518 (1932). More recently, Norrish, *Acta Physicochim. U.R.S.S.*, **3**, 73 (1935); *Trans. Faraday Soc.*, **30**, 105 (1934); *Proc. Roy. Soc. (London)*, **A146**, 257 (1934), has expressed a different view.

⁷⁴ The reaction $RCHO^* + RCHO \rightarrow 2RH + 2CO$ is also improbable. See § 5.8.

⁷⁵ Patat, *Z. physik. Chem.*, **B25**, 208 (1934); Löcker and Patat, *ibid.*, **B27**, 431 (1934). Free H atoms seem to be formed only at $< 2700 \text{ \AA}$. The beginning of the diffuse region at $2750 \text{ \AA}$ corresponds to ~ 103 kcal. per mole; cf. the strength of the C—H bond. See also the work of Norrish and Noyes, *Proc. Roy. Soc. (London)*, **A163**, 221 (1937) at $\lambda < 1600 \text{ \AA}$.

⁷⁶ Akeroyd and Norrish, *J. Chem. Soc.*, 890 (1936).

⁷⁷ Pearson and Purcell, *J. Chem. Soc.*, 1151 (1935); cf. Burton, *J. Am. Chem. Soc.*, **58**, 1655 (1936).

aldehydes is indirect and based largely on analyses of the products. The results show that reaction (6), as compared with reaction (8) below, is favored by a decrease in the wave length of the active light.⁷⁸ According to Burton and Rollefson⁷⁰ it probably does not occur above $\sim 2750 \text{ \AA}$ for formaldehyde, or above $\sim 3150 \text{ \AA}$ for the higher aldehydes.⁷⁹ The free radicals so formed enter into subsequent reactions. Although the HCO radical is stable at 100° ,⁸⁰ it may decompose at higher temperatures, according to the reaction



Any atoms so formed and the free radicals formed in reaction (6) probably enter into subsequent reactions, such as



When R is a radical, the RCO may decompose, yielding the free radical and CO. Thus we see that (6b) is a chain reaction in the case of the higher aldehydes at relatively low temperatures.⁸¹

Historically, reaction (6b) is very important since much of the evidence for the free radical chain theory of Rice and Herzfeld⁸² was derived from experiments in which chains were produced in acetaldehyde by the deliberate introduction of free radicals⁸³ and in which the quantum yield of the photolysis at different temperatures was determined.⁸⁴ As may be expected from the fact that reaction (6b) has

⁷⁸ Both Patat and Sachsse, *Z. physik. Chem.*, **B31**, 106 (1935), and Rollefson, *J. Phys. Chem.*, **41**, 259 (1937), have shown that in the event of competition between decompositions into free radicals and into stable molecules the former is favored by decrease in wave length. Cf. Rollefson and Burton, *J. Chem. Phys.*, **6**, 674 (1938).

⁷⁹ Here $3050 \text{ \AA}$ (corresponding to $\sim 93 \text{ kcal. per mole}$) is the beginning of the diffuse region of acetaldehyde; cf. the strength of the C—C bond.

⁸⁰ Burton, *J. Am. Chem. Soc.*, **58**, 1655 (1936); *J. Phys. Chem.*, **41**, 322 (1937); *J. Am. Chem. Soc.*, **60**, 212 (1938).

⁸¹ According to Spence and Wild, *J. Chem. Soc.*, **352** (1937), CH_3CO is unstable at 60° . CH_3CO also disappears by the reaction $2\text{CH}_3\text{CO} \rightarrow (\text{CH}_3\text{CO})_2$.

⁸² Rice and Herzfeld, *J. Am. Chem. Soc.*, **56**, 284 (1934).

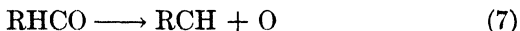
⁸³ Allen and Sickman, *ibid.*, **56**, 2031 (1934).

⁸⁴ Leermakers, *J. Am. Chem. Soc.*, **56**, 1537 (1934); Akeroyd and Norrish, *J. Chem. Soc.*, 890 (1936).

an energy of activation (see Table 33, Appendix III), the quantum yield increases with temperature. For formaldehyde, it is 100 at 350°; for acetaldehyde, Leermakers gives a figure of 300 at 309.5°. At ordinary temperatures it is likely that the HCO radicals disappear by one of these reactions:



As for the alkyl radicals, the reactions by which they disappear depend on their length. For example, free radicals (e.g., CH_3^{86}) combine but rarely, even in a three-body collision, to form alkanes. On the other hand, possibilities of combination and disproportionation of free alkyl radicals are increased with the size of the radical. This subject is discussed more fully in § 5.5. Another type of decomposition into free radicals



is excluded on energetic grounds. This may be seen more clearly in the case of formaldehyde (where $\text{R} = \text{H}$). The atomic heat of formation of HCHO is ~ 339 kcal. The atomic heat of formation of CH_2 is ~ 180 kcal.; i.e., approximately twice the average heat of formation of the C—H bond in methane. Therefore the energy required for reaction (3) is ~ 159 kcal., or much more than that available at the beginning of the photoactive region of the spectrum.⁸⁷

Decomposition into ultimate molecules



appears to take place throughout the whole first absorption region of all the aldehydes. Herzberg and Franz⁸⁸ state that, in formaldehyde, addition of air up to 100 mm. pres-

⁸⁵ Farkas and Sachsse, *Z. physik. Chem.*, **B27**, 111 (1934); Frankenburger, Klinkhardt, Steigerwald, and Zimmermann, *Z. Elektrochem.*, **36**, 757 (1930).

⁸⁶ Blacet and Volman, *J. Am. Chem. Soc.*, **60**, 1243 (1938), have suggested that reaction (6e) is important in the case of acetaldehyde.

⁸⁷ Mecke, *Nature*, **125**, 526 (1930).

⁸⁸ Herzberg and Franz, *Z. Physik*, **76**, 720 (1932).

sure does not diminish the fluorescence appreciably. This indicates that collisions with nitrogen or oxygen molecules neither dissipate the energy of the excited formaldehyde molecules nor induce decomposition. It may consequently be inferred that at 3530–3270 Å, at any rate, the mechanism is a slow spontaneous predissociation.⁷⁰

In the case of acetaldehyde and propionaldehyde, there is actually a slight decrease of quantum yield with pressure at 3130 Å. Although such evidence is not conclusive, it is compatible with the assumption of the spontaneous predissociation process, reaction (8); there is no good evidence for a reaction, such as (5), in any case. An increase in quantum yield with pressure, also at 3130 Å, noted in the case of *n*-butyraldehyde is possibly to be attributed to reaction (5).

Norrish and Bamford⁸⁹ have indicated that, for molecules with sufficiently long chains, the reaction



is also to be expected.⁹⁰ This reaction has been verified by Leighton, Levanas, Blacet, and Rowe in the case of *n*-butyraldehyde, which in this respect behaves quite differently from the *iso* compound. They have also shown that, with decreasing wave length, reaction (9) seems to be completely eliminated as a path of photolysis of the normal compound. In the case of isovaleryl aldehyde, Bamford and Norrish⁹¹ state that 53 per cent of the decomposition proceeds via the primary step



On the basis of the data available, we may draw these conclusions:

(1) In the case of the aliphatic aldehydes, decomposition may take place into ultimate molecules, reaction (8) or

⁸⁹ Norrish and Bamford, *Nature*, **138**, 1016 (1936).

⁹⁰ We write reaction (9) as an induced reaction. It is not so given by Norrish and Bamford.

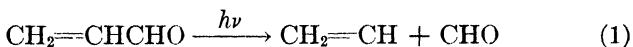
⁹¹ Bamford and Norrish, *J. Chem. Soc.*, 1504 (1935).

(9), throughout the absorption region, and also into free radicals, reaction (6), below wave lengths corresponding roughly to the strengths of the ruptured bonds (i.e., ~ 2750 Å for HCHO and ~ 3150 for the higher aldehydes).⁷⁰

(2) Shift to shorter wave lengths favors decomposition into free radicals.

(3) At ordinary temperatures, in the continuum the quantum yield is of the order of unity. This figure, however, is *very* rough; for more precise information, reference should be made to the original articles, since the effect of pressure as well as of temperature on the quantum yields is also significant.

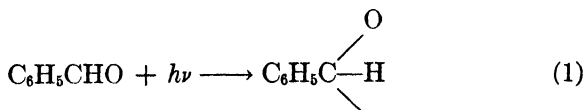
8.73 Unsaturated aliphatic aldehydes. Very little information is available on this class of compounds. The photolysis of acrolein ($\text{CH}_2=\text{CHCHO}$, for example) is complicated by secondary (addition) reactions of the free radicals formed in the decomposition



with other acrolein molecules. The results obtained have been extremely difficult to interpret. Similar remarks may be made concerning crotonaldehyde.⁹²

8.74 Benzaldehyde. Decomposition of $\text{C}_6\text{H}_5\text{CHO}$, yielding chiefly C_6H_6 and CO , occurs only in the diffuse region of the spectrum. The diffuse region is shifted toward longer wave lengths by an increase in temperature. At such elevated temperatures the benzaldehyde decomposes when illuminated in the new diffuse regions.⁹³

According to Bäckström,⁹⁴ $\text{C}_6\text{H}_5\text{CHO}$ illuminated with the full mercury arc yields benzoin, indicating the successive reactions



⁹² See Table 13 for references.

⁹³ De Hemptinne, *Compt. rend.*, **186**, 1295 (1928); Almasy, *J. chim. phys.*, **30**, 713 (1933).

⁹⁴ Bäckström, *Z. physik. Chem.*, **B25**, 99 (1934).

case of ketene, the diffuse nature of the absorption leads to the same conclusion.

TABLE 14
NEAR-ULTRAVIOLET ABSORPTION SPECTRA OF THE VAPORS
OF THE KETONES

Substance	SPECTRUM RANGE, Å			Fluorescence Caused by	Reference
	Discrete	Diffuse	Continuous		
CH ₃ COCH ₃	3340-2945			3130-2536	(1-8), (10), (13)
CH ₃ COC ₂ H ₅			3200-2400	3130	(9)
CH ₃ COC ₄ H ₉			3200-2500		(12)
CH ₂ CO		3850-2601	< ~ 2200		(11), (14)

REFERENCES

- (1) Fisk and Noyes, *J. Chem. Phys.*, **2**, 654 (1934).
- (2) Noyes, Duncan, and Manning, *ibid.*, **2**, 717 (1934).
- (3) Duncan, *ibid.*, **3**, 131 (1935).
- (4) Noyes, *Trans. Faraday Soc.*, **33**, 1495 (1937).
- (5) Norrish and Appleyard, *J. Chem. Soc.*, 874 (1934).
- (6) Bowen and Thompson, *Nature*, **133**, 571 (1934).
- (7) Norrish, *ibid.*, **133**, 837 (1934).
- (8) Norrish, Crone, and Saltmarsh, *J. Chem. Soc.*, 1456 (1934).
- (9) Duncan, Ells, and Noyes, *J. Am. Chem. Soc.*, **58**, 1454 (1936).
- (10) Howe and Noyes, *ibid.*, **58**, 1404 (1936).
- (11) Norrish, Crone, and Saltmarsh, *J. Chem. Soc.*, 1533 (1933); *J. Am. Chem. Soc.*, **56**, 1644 (1934).
- (12) Block and Norrish, *J. Chem. Soc.*, 1638 (1935).
- (13) Matheson and Noyes, *J. Am. Chem. Soc.*, **60**, 1857 (1938), have now shown that the "green fluorescence" formerly attributed to acetone excited at λ 3130-2536 Å is properly attributable to the formation of diacetyl.
- (14) Lardy, *J. chim. phys.*, **21**, 353 (1934).

For details of absorption spectra in the Schumann and far ultraviolet regions, the reader is referred to the papers of Noyes and his co-workers (*v.* Table 14). For acetone, there is a series of discrete bands at 1995-1820 Å; at shorter wave lengths, other bands which fit a Rydberg formula predicting an ionization potential of 10.2 volts; and at still shorter wave lengths, a continuum extending down to the limit of observation at $\sim$ 800 Å.⁹⁷ No fluorescence is excited by light near 1900 Å. For methyl ethyl ketone, there is a

⁹⁷ Howe and Noyes, *J. Am. Chem. Soc.*, **58**, 1404 (1936), have attempted an analysis of the spectrum on the basis of potential energy surfaces.

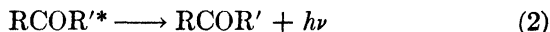
region of discrete bands, broken by short regions of high transmission extending from 1975 to 1550 Å. At still shorter wave lengths there is a continuum extending to the limit of observation at 780 Å. The ionization potential determined by electron bombardment⁹⁸ is 10.5 volts, as compared with 10.1 volts (by the same method) for acetone. The electron removed is described as a non-bonding one associated with the oxygen atom.

8.76 Photochemistry of the ketones. The photochemistry of the ketones is similar to that of the aldehydes (§ 8.72). Like the aldehydes, they absorb in the C=O bond, and rupture of a bond or bonds invariably occurs in some other part of the molecule. Consequently it follows, from our definition of predissociation, that in the ketones decomposition always occurs via some predissociation process. As in the case of the aldehydes, no simple net reaction can be written for the ketones. In the lower ones, mixtures of alkanes and CO are produced; in the higher ones (including the cyclic ketones), simpler ketones and aldehydes, as well as ring compounds and unsaturated products, may be formed. Correspondingly, there are a variety of primary processes.

Simple activation,



where R and R' are either the same or different radicals, occurs as the first step in every part of the absorption region (see Table 14). Only a small amount of the energy is dissipated by *fluorescence*⁹⁹



and *no polymerization* has been reported for the simple ketones. However, the quantum yields reported at ordinary temperatures are uniformly below unity, indicating a high percentage of *collisional deactivation*



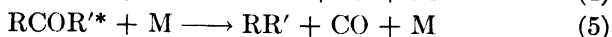
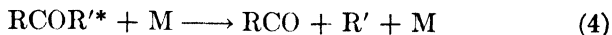
⁹⁸ Noyes, *J. Chem. Phys.*, **3**, 430 (1935).

⁹⁹ Cf. Fisk and Noyes, *J. Chem. Phys.*, **2**, 654 (1934).

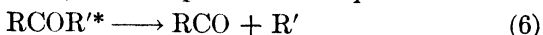
¹⁰⁰ M' is a molecule containing a small excess of energy; M is the same molecule in the normal state.

as well as possible recombination of the decomposition products.

Decomposition processes which may occur include induced predissociation



where either free radicals or ultimate molecules are formed in the primary process; and spontaneous predissociation



In the case of the higher ketones, as in the case of the aldehydes, a reaction may occur in which a stable alkene molecule is produced in the primary step



As might be expected, acetone has been the most thoroughly studied of all the ketones. The formation of alkyl radicals during the photolysis has been established both by the para-ortho hydrogen conversion³² and by mirror methods.¹⁰¹ Using the latter methods, Pearson and his co-workers have shown that such radicals are also produced in the cases of methyl, ethyl, diethyl, methyl propyl, methyl isopropyl, dipropyl, diisopropyl, methylbutyl, di-sec. butyl and di-tert. butyl ketones.¹⁰²

Although it was thought at one time that the primary act was a fission of the molecule into CO and two radicals,¹⁰³ the more recent work of Pearson and his co-workers with the methyl ketones has shown the formation of acetyl radicals. In the case of acetone, there is substantial equivalence between the number of acetyl and methyl radicals formed.¹⁰⁴

¹⁰¹ Pearson, *J. Chem. Soc.*, 1718 (1934); cf. Prileshajeva and Terenin, *Trans. Faraday Soc.*, **31**, 1483 (1935); Burton, *J. Am. Chem. Soc.*, **58**, 1645 (1936).

¹⁰² Pearson and Purcell, *J. Chem. Soc.*, 1151 (1935); 253 (1936). Pearson and Glazebrook, *ibid.*, 1777 (1936); Glazebrook and Pearson, *ibid.*, 567 (1937).

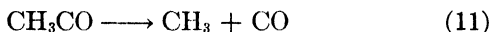
¹⁰³ Norrish and Kirkbride, *Trans. Faraday Soc.*, **30**, 103 (1934); Norrish, Crone, and Saltmarsh, *J. Chem. Soc.*, 1456 (1934).

¹⁰⁴ The slight excess of acetyl radicals reported by Glazebrook and Pearson is perhaps to be attributed to experimental error or even to a reaction of the type $\text{CH}_3\text{COCH}_3^* + \text{CH}_3\text{COCH}_3 \rightarrow \text{C}_2\text{H}_6 + 2\text{CH}_3\text{CO}$. Their experiments showed that it was not to be attributed to a chain reaction involving free methyl radicals.

This was to be expected from the earlier results of Barak and Style,¹⁰⁵ who found diacetyl, $(\text{CH}_3\text{CO})_2$, among the products of the photolysis of acetone; and of Spence and Wild,¹⁰⁶ who made a thorough study of the products of photolysis under varying conditions. It has been shown that at room temperature the primary step in the case of acetone is probably



The various secondary reactions are probably



There is good reason to believe that the ethane is not formed by the combination of two methyl radicals.¹⁰⁷

Above 60° , CH_3CO is so unstable that practically no diacetyl is formed.^{107a} There is indication, based on analytical evidence, that in the discrete region at $3130 \text{ \AA}$ acetone decomposes, with low quantum yield, directly into ultimate molecules in the primary step.¹⁰⁶ The mechanism is probably induced predissociation,⁷⁰ i.e., reaction (5). Assuming that the photolysis goes exclusively by a free radical mechanism, reaction (4) or (6), in the case of acetone,¹⁰⁸ Glazebrook and Pearson have estimated the relative numbers of free radicals produced in the case of the other ketones under like conditions, based on their mirror work; and Norrish and his co-workers have made a similar estimate, based on analyses of the products. The results are shown in Table 15.

It should be emphasized that Glazebrook and Pearson's estimates are based on direct observations of rates of mirror removal, whereas Norrish's involve assumptions as to the way in which the final products are formed. The discrepancy

¹⁰⁵ Barak and Style, *Nature*, **135**, 307 (1935).

¹⁰⁶ Spence and W. Wild, *Nature*, **138**, 206 (1936); *J. Chem. Soc.*, 352 (1937).

¹⁰⁷ Cf. Davis, Jahn, and Burton, *J. Am. Chem. Soc.*, **60**, 10 (1938).

^{107a} Glazebrook and Pearson, *J. Chem. Soc.*, 567 (1937), have verified this conclusion directly by the use of the mirror method.

¹⁰⁸ This assumption is *practically* correct when general radiation of a Hg arc is used.

TABLE 15

ESTIMATE OF THE PER CENT DECOMPOSITION INTO FREE RADICALS IN THE PHOTOLYSIS OF SEVERAL KETONES

Ketone	Glazebrook and Pearson	Norrish et al.
Acetone	100	100
Methyl ethyl	81	70-80
Methyl <i>n</i> -propyl	62	—
Methyl <i>n</i> -butyl	28	10
Di <i>n</i> -propyl	37	37
Di isopropyl	41	44

in the case of methyl butyl ketone¹⁰⁹ may be due to the assumption that reaction (8) is the exclusive source of propylene. It is conceivable, however (though not probable), that some may come from a disproportionation reaction such as $\text{CH}_3 + \text{C}_4\text{H}_9 \rightarrow \text{C}_2\text{H}_6 + \text{C}_3\text{H}_6$. The small discrepancy in the case of methyl ethyl ketone also may be due to the assumption of the mechanism involved. In this case, Norrish and Appleyard have suggested a mechanism



which is somewhat different from reaction (8). However, no direct evidence was presented for the formation of acetaldehyde, and the assumption may be in error.

The quantum yield of the photolysis of acetone is given by Damon and Daniels¹¹⁰ as 0.17 at 56° and atmospheric pressure, in the range 3130-2650 Å. The yield increases at low light intensities, and decreases at low pressures. As the temperature is raised to 396°, the yield increases to 0.76.^{76, 111} At ordinary temperatures and ~1900 Å, the yield approaches a limiting value of 0.65 as the pressure is decreased (to ~0.2 mm.).^{111a}

The higher ketones have been studied principally by

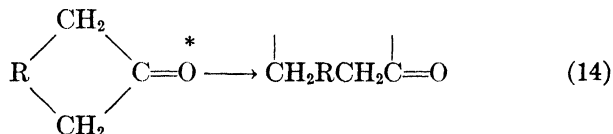
¹⁰⁹ Norrish and Appleyard, *J. Chem. Soc.*, 874 (1934).

¹¹⁰ Damon and Daniels, *J. Am. Chem. Soc.*, **55**, 2363 (1933); cf. Norrish, Crone, and Saltmarsh, *J. Chem. Soc.*, 1456 (1934).

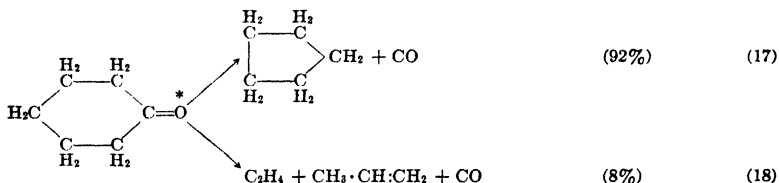
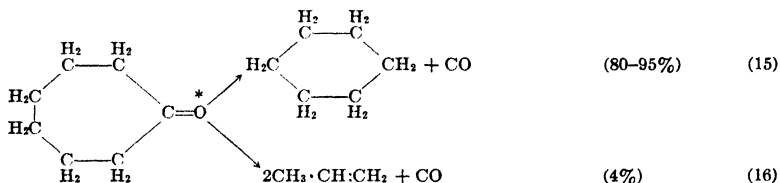
¹¹¹ Cf. Winkle, *Trans. Faraday Soc.*, **31**, 761 (1935).

^{111a} Howe and Noyes, *J. Am. Chem. Soc.*, **58**, 1404 (1936). Manning, *ibid.*, **56**, 2589 (1934), found hydrogen among the products at ~1700 Å.

Norrish, by Pearson, and by Bowen and their co-workers, the latter confining their work mainly to solutions (see § 14.12). The quantum yield is low in all cases.¹¹² In the higher ketones¹¹³ the principal products are formed via path (8).¹¹⁴ The cycloketones,¹¹⁵ on the other hand, probably decompose entirely via a free radical mechanism.¹¹⁶ The investigations of Glazebrook and Pearson¹⁰² on the simpler ketones make it appear probable that the first step in this case is the formation of an acyl di-radical



and that the latter may then rearrange.¹¹⁷ The following overall reactions have been indicated:



¹¹² Cf. Block and Norrish, *J. Chem. Soc.*, 1638 (1935).

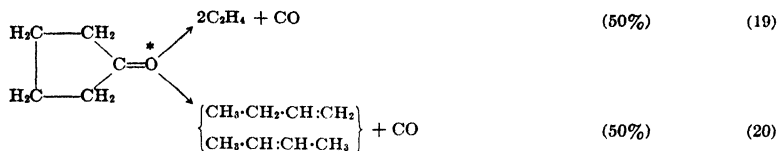
¹¹³ V. also Bamford and Norrish, *J. Chem. Soc.*, 1504 (1935); Norrish and Bamford, *Nature*, **138**, 1016 (1936); **140**, 195 (1937).

¹¹⁴ In the study of diisopropyl ketone, Glazebrook and Pearson, *J. Chem. Soc.*, 1777 (1936), have expressed the opinion that the free isopropyl radical produced tautomerizes to the normal radical either on combination with the lead mirror or immediately thereafter.

¹¹⁵ V. Forster, Skrabal, and Wagner, *Z. Elektrochem.*, **43**, 290 (1937), for the absorption spectra of cycloketones in hexane solution.

¹¹⁶ Saltmarsh and Norrish, *J. Chem. Soc.*, 455 (1935); Norrish, *Acta Physicochim.*, U.R.S.S., **3**, 171 (1935).

¹¹⁷ Norrish, *Trans. Faraday Soc.*, **30**, 103 (1934), has pointed out, contrariwise, that the reorganization of the carbonyl group $\text{C}=\text{O}$ to carbon monoxide ($\text{C}=\text{O}$) yields 101 kcal., which is more than sufficient to permit the simultaneous rupture of both bonds in the excited molecule.



A simple interpretation of the results would involve the idea that oscillation of the radical $\text{CH}_2-\text{R}-\text{CH}_2-\text{C}=\text{O}$ ends in an internal collision of the CH_2 tail with the CH_2-CO bond, resulting in rupture of the latter and closure of the ring. Unless this occurs more frequently than the competing process, in which the CH_2-CO bond is broken as the result of an external effect (e.g., a collision), a radical $\text{CH}_2\cdot\text{R}\cdot\text{CH}_2$ is formed. The latter is stabilized by shift of a hydrogen atom or by rupture. Judging from the three cases cited above, we see that the hydrogen atom may be shifted readily a distance of one or two carbon atoms, but not to a third.¹¹⁸

The quantum yield of the photolysis of ketene at 3700 Å is 1.0. The products are CO and C_2H_4 .¹¹⁹ Ross and Kistiakowsky have suggested that the primary reaction is the decomposition into CO and CH_2 . The CH_2 groups may react with each other, or with C_2H_4 molecules previously formed, ultimately building up into a solid polymer.

Another compound of interest in connection with the ketones is acetyl acetone, which polymerizes but yields no CO at 3030 Å.¹²⁰ At lower wave lengths CO is produced.

8.8 Fatty acids. As seen from Fig. 43¹²¹ (p. 240), all the fatty acids are similar in that the absorption spectrum begins at 2400–2300 Å.¹²² The extinction reaches a maximum at 2040 Å, falls off slightly, and then continues to increase to the limit of observation at 1850 Å. Except for formic acid,

¹¹⁸ Saltmarsh and Norrish have proposed a different explanation of these reactions, based on the thermal stability of the cycloparaffins.

¹¹⁹ Ross and Kistiakowsky, *J. Am. Chem. Soc.*, **56**, 1112 (1934).

¹²⁰ Perez Vitoria, *IX Congr. intern. quim. pura aplicada*, **2**, 334 (1934).

¹²¹ Ley and Arends, *Z. physik. Chem.*, **B4**, 234 (1929); **B17**, 177 (1932). Cf. Henri, *Etudes de Photochimie*, Gauthier-Villars et Cie., Paris, 1919, p. 90; Hantzsch, *Ber.*, **59**, 1096 (1926).

¹²² The absorption spectrum of formic acid begins at 2500 Å.

the absorption is in all cases apparently continuous. Although at room temperature and 35 mm. pressure the absorption spectrum of that acid is continuous, at 100° and 25 mm.

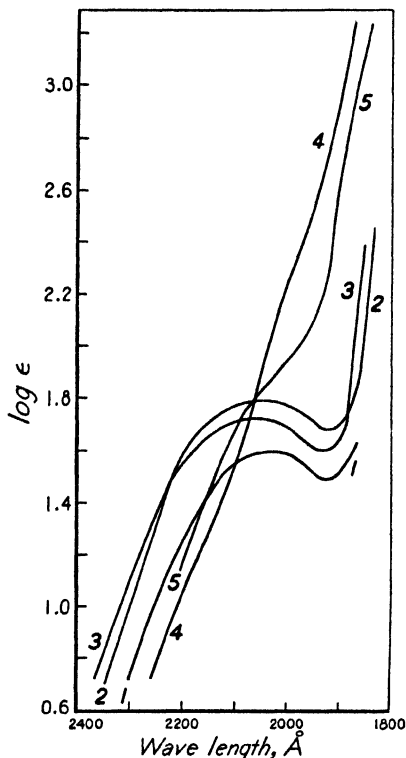


Fig. 43. Extinction Coefficients of the Fatty Acids, according to Ley and Arends, *Z. physik. Chem.*, **B17**, 177 (1932). $\epsilon = \frac{1}{cl} \log \frac{I_0}{I}$. (1) Acetic acid. (2) Butyric acid. (3) Formic acid. (4) Sodium acetate in water. (5) Sodium formate in water.

it is strongly banded.¹²³ All the monobasic acids have a tendency to dimerize through the formation of hydrogen bridges; the vapor as well as the solutions in hexane, for example, consists largely of dimeric molecules and a lesser amount of the monomer.¹²⁴ In the dimer, the two carboxyl groups join to form an eight-membered plane ring.¹²⁵ According to Gorin and Taylor,¹²³ the diffuse bands in the absorption spectrum of formic acid are due to the monomer, whereas the apparent continuum is due to the dimer.

Since the absorption spectrum of the esters follows a similar course,¹²⁶ the absorption in the case of the acids must be attributed to the presence of a group common to all cases; namely, the CO_2 group.¹²⁷ The decomposition, which follows absorption in any

¹²³ E. Gorin and H. S. Taylor, *J. Am. Chem. Soc.*, **56**, 2042 (1934).

¹²⁴ For the case of acetic acid, cf. MacDougall, *J. Am. Chem. Soc.*, **58**, 2585 (1936).

¹²⁵ Gillette and A. Sherman, *J. Am. Chem. Soc.*, **58**, 1135 (1936).

¹²⁶ Ley and Arends, *Z. physik. Chem.*, **B17**, 177 (1932).

¹²⁷ For a discussion of a similar case, see the aldehydes and ketones, § 8.7.

part of the region described, involves a possible rupture of that group only in the case of formic acid. It follows (see § 4.3) that photolysis of these acids always occurs via a predissociation mechanism.

The following discussion applies only to the monobasic acids. The polybasic acids are discussed at the end of this section and in the chapter on solutions (§ 14.7). The products of photolysis include mixtures of alkanes (except for formic acid), CO, CO₂, H₂O, H₂, and traces of C₂H₂. The first step in all cases is simple activation:



where R may be a hydrogen atom or an aliphatic radical. No fluorescence has been reported. The reported values of ~ 1.0 for the quantum yield in the cases of formic¹²⁹ and acetic acids¹³⁰ suggest that there is very little, if any, collisional deactivation.

The *decomposition* processes vary, depending on the nature of R in RCOOH and on whether the monomer or the dimer is involved. In the case of formic acid, the following reactions may occur:



No atomic hydrogen has been detected in the photolysis of formic acid either by the para-ortho hydrogen conversion method¹²³ or by the mirror method;¹³¹ but hydroxyl radicals have been detected by their emission spectrum when the

¹²⁸ In this section unprimed reactions are characteristic of both monomer and dimer. Reactions marked (') are characteristic of the *monomer*; those marked (') are characteristic of the *dimer*.

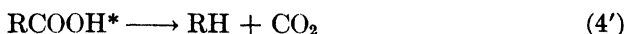
¹²⁹ Gorin and Taylor, *loc. cit.* The value is based on the number of single molecules decomposed.

¹³⁰ L. Farkas and Wansbrough-Jones, *Z. physik. Chem.*, **B18**, 124 (1932). The value is based on the number of alkane molecules formed.

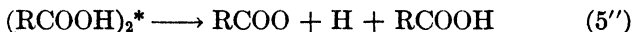
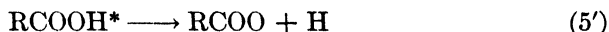
¹³¹ Burton, *J. Am. Chem. Soc.*, **58**, 1655 (1936).

photolysis is conducted at $\sim 1560 \text{ \AA}$.⁶³ Since the last method is extremely sensitive to traces of hydroxyl⁶⁴ and the para-ortho method is sensitive to any free radical or atom, it must be concluded that, in the wave length region used for the chemical investigation (2540–1900 $\text{\AA}$), ultimate molecules are formed in the primary act.¹³²

In the case of acetic acid vapor, Farkas and Wansbrough-Jones¹³⁰ suggest these overall reactions:



That the reaction is somewhat more complicated than indicated by (4) is shown by their own observation that C_2H_2 and H_2 may also be detected among the products, and by the observation of Burton¹³³ (employing the guard mirror method) that atomic hydrogen is formed during the photolysis. The production of H atoms, presumably by the primary reactions



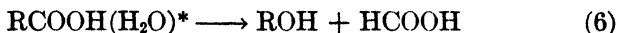
is favored by decrease in wave length. No free alkyl radicals are formed. Here again, Terenin and Neujmin⁶³ have detected hydroxyl radicals at $\sim 1540 \text{ \AA}$, but it is improbable that they are formed in significant quantity in the range of chemical study (2300–1850 $\text{\AA}$). Burton¹³³ has shown that it is possible to explain both quantum yields and products in this case entirely by an exclusive free radical mechanism. However, the increase of atomic hydrogen production at low wave lengths suggests that we have to deal with competition between the primary mechanisms (4) and (5).⁷⁸

In aqueous solution, the acetic acid molecules are 4 per cent dissociated into ions; the remainder are present as

¹³² In aqueous solution, no hydrogen is produced, as by reaction (3), but an additional HCOOH molecule is reduced to formaldehyde. The result suggests a much more complicated reaction.

¹³³ Burton, *J. Am. Chem. Soc.*, **58**, 1645 (1936).

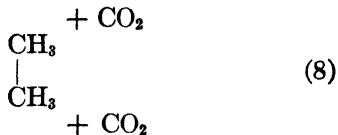
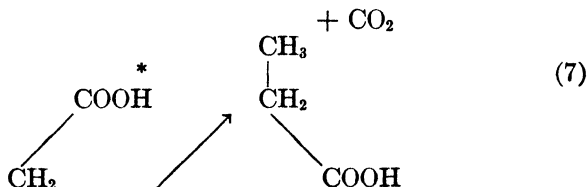
monomer, which decomposes partly according to reaction (4') and partly according to the scheme



resulting ultimately in the interaction of the products of (6) to form an ester. In hexane solution, the results are further complicated by secondary reactions between the primary products and the solvent.

The decomposition of propionic acid in aqueous solution proceeds via both the overall reactions (4') and (6).^{130, 134} However, the detection, by the mirror method, of atomic hydrogen (but no alkyl radicals) in the photolysis of the vapor indicates that the actual course of the reaction may be somewhat more complicated.¹³⁵ More than 2.3 times as many hydrogen atoms are produced per einstein absorbed in this case as are produced in that of acetic acid.

As for the dibasic acids, the absorption spectrum of succinic acid in aqueous solution is similar to that of acetic acid.¹²¹ The photolysis yields, in addition to esters (cf. reaction 6), gaseous products by the alternative reactions



In this series oxalic acid behaves abnormally.¹³⁶ The absorp-

¹³⁴ Pierce and Morey, *ibid.*, **54**, 467 (1932).

¹³⁵ Henkin and Burton, *ibid.*, **60**, 831 (1938).

¹³⁶ Allmand and Reeve, *J. Chem. Soc.*, 2834, 2852 (1926).

tion sets in at longer wave lengths (cf. formic acid); the mechanism of the photolysis in solution is confused by the fact that we are here dealing with a relatively strong acid so that both ions and molecules are involved. Also, unlike the other carboxylic acids discussed, oxalic acid contains conjugated double bonds. CO, CO₂, and H₂O are produced by the photolysis.

Since the salts of the fatty acids are dissociated into ions in aqueous solution, it is evident that their photochemical behavior is essentially different from that of the acids (cf. the absorption spectrum, Fig. 43). The case of fumaric and maleic acids is discussed more properly in the chapter on rearrangements (§ 9.22).

8.81 Esters. The absorption spectra of the aliphatic esters are similar to those of the fatty acids¹³⁷ (cf. § 8.8). No photochemical investigations are reported.

8.82 Acetyl halides. Etzler¹³⁸ has studied the absorption spectra and photochemical decompositions of acetylchloride, bromide, and iodide. The absorption coefficients are listed in Table 16.

TABLE 16
ABSORPTION COEFFICIENTS OF THE ACETYL HALIDES

$$\epsilon = \frac{1}{cl} \log \frac{I}{I_0} \quad (c \text{ in moles/liter, } l \text{ in cm.})$$

Wave Length Å	Chloride	Bromide	Iodide
2537	21.6	64.8	468
2652	10.3	46.8	324
2699	9.2	30.6	—
2753	4.5	12.6	216
2804	2.9	5.0	—
2894	—	—	126
3130	—	—	46.8
3650	—	—	6.5

¹³⁷ Ley and Arends, *Z. physik. Chem.*, **B17**, 177 (1932).

¹³⁸ Etzler, Ph.D. Thesis, University of California, 1938, and forthcoming publications.

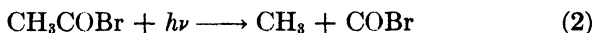
All of these compounds decompose as a result of the light absorption. The products formed indicate that the reactions are not simple. In every case the non-condensable gases consist of a mixture of carbon monoxide and methane. In addition, an alkyl halide, CH_3X , is always formed in relatively large amount. Other products were identified as follows:

From acetyl chloride: HCl and a non-volatile liquid which precipitates during the reaction. An analysis of this liquid indicates that it is a polymer of diacetyl.

From acetyl bromide: traces of bromine, and some substances containing more than one atom of bromine per molecule.

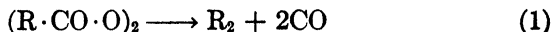
From acetyl iodide: iodine and a liquid (probably the same as found with acetyl chloride).

The quantum yield for the bromide decomposition was found to be approximately 0.5. In order to account for the products and the effect of NO on the system, it was found necessary to assume at least three parallel primary steps. They are:



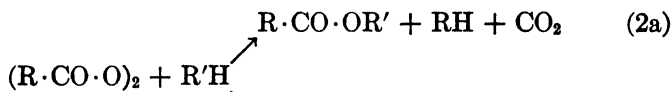
Further work must be done with the chloride and iodide before it can be said whether or not there are similar steps in those decompositions.

8.83 Acyl peroxides. The absorption spectra of these compounds begin at longer wave lengths than do those of the corresponding acids. For example, the spectrum of $(\text{CH}_3\text{COO})_2$ dissolved in hexane begins at $\sim 2750 \text{ \AA}$.¹³⁹ In general, either pyrolysis or photolysis of these compounds yields a large variety of products. The main course of the reaction is:



¹³⁹ O. J. Walker and G. L. E. Wild, *J. Chem. Soc.*, 1132 (1937).

accompanied by



where $R'H$ may be a molecule of solvent or peroxide, or of one of the decomposition products.¹⁴⁰

TABLE 17

PHOTOCHEMISTRY OF THE METALLO-ORGANIC COMPOUNDS

Substance	Continuum Å	Absorption Maximum Å	λ Å	γ	Reference
Hg(CH ₃) ₂	<2600	2040	2537	~ 1	(1-4), (7)
		1660			
Hg(C ₂ H ₅) ₂	—	2250	—	—	(3)
		1955			
CH ₃ HgBr	—	—	—	—	(6)
CH ₃ HgI	—	—	—	—	(6)
C ₂ H ₅ HgCl	—	2366	—	—	(3)
Hg(C ₆ H ₅) ₂	—	2600	—	—	(3)
C ₆ H ₅ HgCl	—	2595	—	—	(3)
		2378			
Pb(CH ₃) ₄	<2800	—	See Table 23.	—	(5)
Pb(C ₂ H ₅) ₄	<3500	~ 2000	—	—	(5-7)
Pb(C ₆ H ₅) ₄	<2800	2550	—	~ 0.23 in C ₆ H ₆	(5)
Zn(CH ₃) ₂	2650-2150	~ 2300	—	—	(6)
Fe(CO) ₅	<4100	—	See Table 22.	—	(8)
Ni(CO) ₄	<3950	—	See Table 24.	—	(8), (9)

REFERENCES

- (1) Linnett and Thompson, *Trans. Faraday Soc.*, **33**, 501 (1937).
- (2) Thompson and Linnett, *ibid.*, **33**, 874 (1937).
- (3) Asundi, Rao, and Samuel, *Proc. Indian Acad. Sci.*, **1A**, 542 (1935).
- (4) Terenin and Prileshajeva, *Trans. Faraday Soc.*, **31**, 1483 (1935).
- (5) Leighton and Mortensen, *J. Am. Chem. Soc.*, **58**, 448 (1936).
- (6) Terenin and Prileshajeva, *Acta Physicochim. U.R.S.S.*, **1**, 759 (1934) (in English); *J. Phys. Chem. (U.S.S.R.)*, **5**, 1004 (1934) (in Russian).
- (7) Terenin, *J. Chem. Phys.*, **2**, 441 (1934).
- (8) Thompson and Garratt, *J. Chem. Soc.*, 524 (1934).
- (9) Garratt and Thompson, *ibid.*, 1817 (1934).

¹⁴⁰ Cf. Gelissen and Hermans, *Ber.*, **59**, 662 (1926); Boeseken and Hermans, *Ann.*, **519**, 133 (1935).

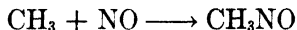
Although qualitatively similar, the products are quantitatively different in the two cases. There is some evidence that the products conform more closely to a reaction of type (1) when the photolysis is conducted at ordinary temperature,¹⁴¹ although the ensuing reactions (2a) and (2b) definitely contribute to the complexity of the yield.¹⁴²

8.9 Metallo-organic compounds. The principal metallo-organic compounds which have been subjected to photochemical study are the alkyls, the aryls, and the carbonyls. Their absorption spectra, as well as the little photochemical information available concerning them, are summarized in Table 17.

The particularly noteworthy experiments are those on lead tetramethyl and mercury dimethyl. In the former, Leighton and Mortensen detected the presence of free methyl radicals by streaming the products of the photolysis over radioactive lead mirrors and detecting the loss in the radioactivity of the lead mirror caused by the formation of volatile $\text{Pb}(\text{CH}_3)_4$ in the reaction



In the work on mercury dimethyl, Thompson and Linnett detected the formation of free methyl radicals by their reaction with nitric oxide



The latter product is assumed to rearrange, yielding a solid product (polymerized formaldoxime). The method of experiment was to compare the pressure changes observed during photolyses in the absence and in the presence of nitric oxide.

¹⁴¹ Walker, *J. Chem. Soc.*, 2040 (1928); Walker and Wild, *ibid.*, 207 (1935); Fichter and Schnider, *Helv. Chim. Acta*, **13**, 1428 (1930).

¹⁴² For acetyl benzoyl peroxide, v. Fichter and Willi, *Helv. Chim. Acta*, **17**, 1173 (1934); for acetyl peroxide, v. Walker and Wild, *J. Chem. Soc.*, 1132 (1937).

CHAPTER IX

MOLECULAR REARRANGEMENTS

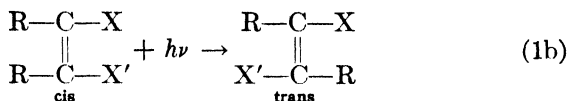
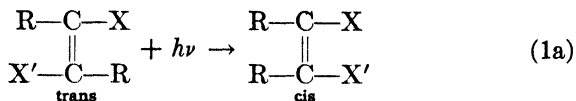
9.1 Types of intramolecular change. For the purposes of this chapter we shall classify internal rearrangements of the molecule into three types: rotation about a double bond, interchange of two atoms within a molecule, and shift of a single atom or a group within a molecule. Some tautomeric changes occur readily at ordinary temperatures (e.g., the *keto-enol* reaction) and consequently have not been studied photochemically. In the case of *cis-trans* isomerism, on the other hand, it has been found that illumination with ultraviolet light has a definite effect on the nature of the equilibrium. Such cases are discussed in the section on rotation about a double bond (§ 9.2).

Internal rearrangements have been investigated both as to their mechanism¹ and as to their kinetics.² Their peculiar interest lies in the fact that they may occur without the assistance of a second molecule. Although intermediate dissociation and recombination have been postulated to account for the effects observed, simple interchange within that fuzzy region which may be called the molecular diameter is also a possibility. It is because these reactions may offer an insight into simple intramolecular mechanisms and *unimolecular processes* that they have been studied so extensively. In this chapter we shall consider only reactions which are apparently simple, although, as will be seen, they may not be unimolecular. The subject of photosensitized rearrangements is reserved for later discussion (§§ 10.63, 10.68).

9.2 Rotation about a double bond. Studies of the effect of ultraviolet light on isomerization reactions of the type

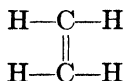
¹ Porter, *Molecular Rearrangements*, Reinhold Publishing Corp., New York, 1928.

² Cf. Kistiakowsky and Smith, *J. Am. Chem. Soc.*, **58**, 766, 2428 (1936).



where X' may be the same as X, have been studied for many years. Stoermer³ showed that, with many pairs of stereoisomers, the ratio of the components approached a limiting value under prolonged ultraviolet illumination. Since in such photostationary states the less stable isomer is always present in excess, the action of the light cannot be likened to that of a simple catalyst. Many other studies of such reactions, including the quantum efficiencies at various wave lengths and the effect of temperature, have been made. Because the experimental results appear to be confusing, we shall defer consideration of them and examine first a model suggested by Olson,⁴ which has assisted in the clarification of this whole subject.

9.21 Olson's model. In the case of the simple ethylene molecule



assume that the lower half is in the plane of the paper. The energy required to rotate the upper half of the molecule about the double bond may be represented by a curve of the type shown in Fig. 44 (p. 250). If, as appears both from chemical and quantum mechanical considerations,⁵ the two HCH radicals are in the same plane at ordinary temperatures, there is evidently a potential energy barrier to their free rotation about the double bond. A minimum occurs

³ Stoermer, *Ber.*, **44**, 637 (1911). Cf. Stoermer and Simon, *ibid.*, **37**, 4163 (1904); Stoermer, *ibid.*, **42**, 4865 (1909); **44**, 1853 (1911); **47**, 1786, 1793 (1914).

⁴ (a) Olson, *Trans. Faraday Soc.*, **27**, 69 (1931); (b) Olson and Hudson, *J. Am. Chem. Soc.*, **55**, 1410 (1933); (c) Olson, *J. Chem. Phys.*, **1**, 418 (1933); (d) Olson and Maroney, *J. Am. Chem. Soc.*, **56**, 1320 (1934).

⁵ Cf. Hückel, *Z. Physik*, **60**, 423 (1930).

every 180° . Since the *cis* and *trans* forms of this compound are identical, the minima are at equal energy levels.

However, if one H atom on each of the C atoms is replaced by a radical R, there will now be a slight tendency for the two to repel each other. Thus the *trans* state may be thermodynamically the more stable.⁶ A rotation of the molecule from this state will also require the surmounting of a potential energy barrier in the region where the planes of the two halves are perpendicular to each other. Beyond this

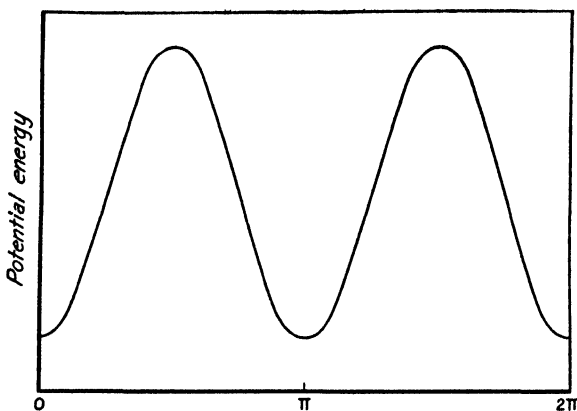


Fig. 44. Potential Energy of an Ethylene Molecule as a function of the relative angular displacement of the two HCH radicals.

point, the potential energy again decreases and there is a minimum when the two halves are again in the same plane.⁷ However, since this is now the *cis* modification, the repulsion of the two R groups causes the potential energy at the minimum to be somewhat higher. The potential energy diagram is shown in Fig. 45. The line *AA* represents the

⁶ Offhand, it would seem that the *trans* state is always the more stable. Actually, due to polarizing effects, the *cis* state may be the one of lower energy content. A case in point is that of the dichloroethylenes. Cf. Stuart, *Molekülstruktur*, Julius Springer, Berlin, 1934, p. 95; *Physik. Z.*, **32**, 793 (1931).

⁷ This is an oversimplified statement. In actual cases there may be slight attractions or repulsions so that there are actually two minima, at either *cis* or *trans* positions or both, the two halves of the molecule being slightly twisted out of a plane. In the original papers Olson has given detailed consideration to such factors.

energy of oscillation of the two halves of the *trans* molecule about the equilibrium position, and the line *BB* represents the energy condition in a molecule oscillating at a level corresponding to a temperature somewhat higher. Similar levels, *CC*, etc., exist for the *cis* molecule.⁸

The vertical difference between the two minima in Fig. 45 is approximately equal to the ordinary *heat of transition* between the *cis* and *trans* forms. The height of the barrier above the average energy level of a given form is evidently

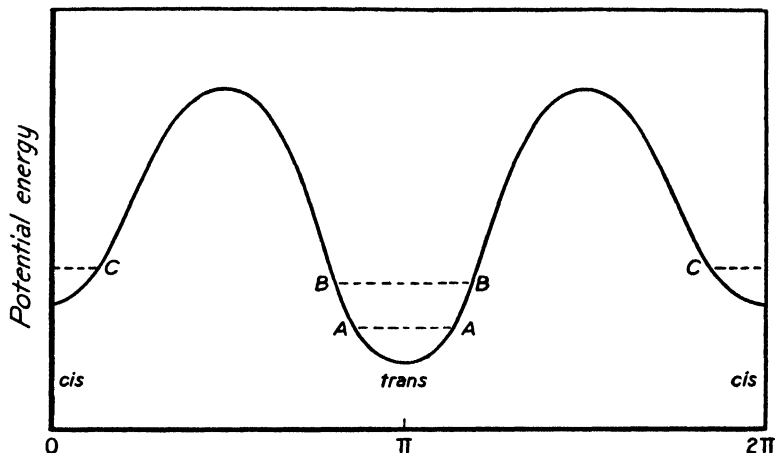


Fig. 45. Potential Energy of $\text{RHC}=\text{CHR}$ as a function of the relative angular displacement of the two RCH radicals.

the energy of activation of the transition. At sufficiently high temperatures many of the molecules will receive enough rotational energy to make them pass over the barrier. In sufficient time the number passing over the barrier in one direction will equal the number passing in the other, and a condition of equilibrium will be attained. The thermal equilibrium point will depend on the heat of transition and,

⁸ The reader must bear in mind that these potential energy diagrams apply only to rotations. The oscillations referred to are *twists* of the molecule about a central position. Vibrational energy levels for the condition of the two parts periodically approaching and receding from each other are shown, not in this type of diagram, but in a type similar to Fig. 13. We are not concerned with such levels in this case.

obviously, at that point the *trans* molecules will be present in excess.

However, the mechanism just indicated does not explain the photochemical transition. It has already been shown that it is extremely improbable that a molecule absorbs enough vibrational energy from radiation for dissociation to occur (§ 2.32). Presumably, similar selection rules apply to this case also. The first step in the process of photorearrangement is excitation to a higher electronic level, as shown in Fig. 46. For brevity, all the molecules in a particular state

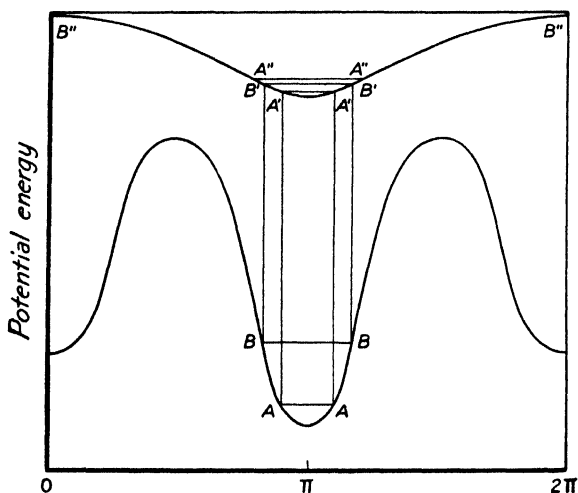


Fig. 46. Potential Energy Curves for Normal and Activated Molecules as a function of angular displacement.

of electron excitation are represented as being on the average energy level corresponding to different temperatures, and vice versa. Considering the *trans* molecule, it is seen that the molecule is symmetrical, and that the minima of the excited and unexcited states consequently occur at the same angle. Since the curves are correspondingly symmetrical about that point, the amplitude of the oscillation is not changed by the electron excitation. On the other hand, the electron excitation in the double bond weakens the restraints on the rotation; i.e., in the upper state the potential energy

barrier restricting free rotation is lower, relatively, than in the lower state. In consequence the upper curve has a more gradual slope, and the oscillational energy is now less than the average energy per degree of freedom corresponding to the temperature.

On excitation at a particular temperature the energy level of the molecule is shifted from AA on the lower curve to $A'A'$ on the upper curve. The excited molecule may then enter into the following processes:

(a) It may return to the ground state with the emission of a photon of the exciting frequency.

(b) It may return to the ground state with the emission of a photon of a modified frequency.

(c) It may give up its energy to other molecules in collisions (i.e., collisions of the second kind) and return to the ground state.

(d) It may acquire additional oscillational energy from other molecules and thus be promoted to a higher level, as $A''A''$. The possibility of this last occurrence is rather high, since it has already been shown that the level $A'A'$ is relatively lower than AA , which corresponds to the temperature equilibrium.

(e) The molecule at the level $A''A''$ does not have sufficient energy to go to the *cis* form. It may return to its ground state by paths (b) or (c).

If now we consider the same molecule at some higher temperature corresponding to BB , it is seen that on electron excitation its energy corresponds to a level $B'B'$. As before, possibilities similar to (a), (b), (c), and (d) occur. However, the level $B''B''$ is sufficiently high that the molecule may now be considered in a condition where the two parts $R-C-H$ execute complete rotations in respect to each other. Since the potential energy at the angle of rotation corresponding to the *cis* form is higher (because of repulsion of the two R groups) than that of the *trans* form, the molecule rotates more slowly during the portion of its rotation corresponding to the former; i.e., in a level such as $B''B''$ the molecule is, most of the time, in the excited condition cor-

responding to the *cis* state. If the probability of return of the molecule to the ground state by photon emission is independent of the angle between its two halves, then the process just described will favor the reaction *trans* $\rightarrow$ *cis*.

At some still higher temperature the molecule will be rotating so fast (i.e., its actual rotational level will be so far above the potential energy barrier) that the times spent in the *cis* and *trans* states will be almost equal. Under such conditions, since it is obvious that *cis* as well as *trans* molecules may be excited by photon absorption, neither of the reactions *trans* $\rightarrow$ *cis* nor *cis* $\rightarrow$ *trans* will be favored, and at sufficiently high temperatures the yield will consist of equimolecular proportions of the two substances.⁹ The relation is shown in Fig. 47.

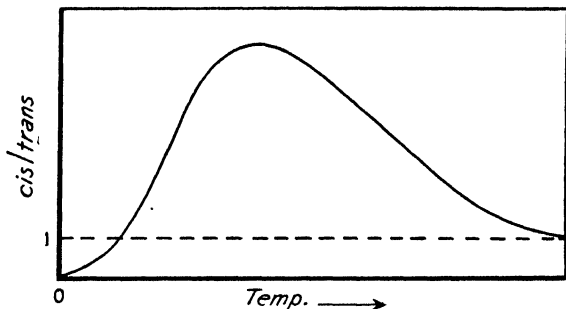


Fig. 47. Variation of the *Cis/Trans* Ratio with Temperature, according to Olson's Model.

As for the effect of *pressure*, it is apparent that low pressures should favor processes (a) and (b), whereas high pressures favor (c) or (d), depending upon the nature of the molecules. If the pressure is due to inert molecules, the establishment of thermal equilibrium will be the predominating effect and process (d) will thus be favored. On the other hand, molecules which quench the fluorescence markedly may favor process (c).

⁹ It must be emphasized that in this statement there exists the implicit assumption that both molecules absorb with equal efficiency (i.e., have the same extinction coefficients) at the wave lengths used.

Variation of *light frequency* is effective in several ways. Small changes in frequency may affect the efficiency of light absorption as well as the precise oscillational level to which the molecule is promoted. However, such effects are of a minor nature and require no amplification of the model for their understanding. A large frequency increase, on the other hand, may be sufficient to cause excitation of the molecule to a higher electronic level.

Referring to Fig. 48, we see that a low frequency may be

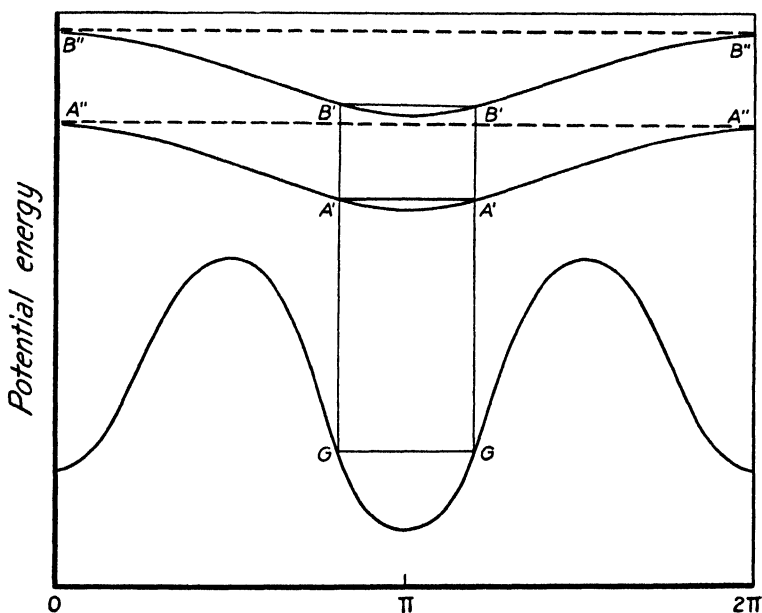


Fig. 48. Potential Energy Curves for a Normal Molecule and for Two Activated States.

sufficient for excitation of the molecule from the ground state GG to a point on the A level, and that a higher frequency is required for excitation to the B level. If the reactions so caused are studied at low pressure, differences will be observed in the fluorescent light, due simply to the fact that light is emitted from different levels in the two cases. On the other hand, since the “shapes” of the excited

levels are similar, practically no change in the *cis/trans* ratio will be noticed. At higher pressures, the influence of other factors must be considered. On activation with light of low frequency, the molecule may be promoted from the ground state *GG* to the state *A'A'*. For simplicity, let us assume that about 10 per cent of these molecules acquire thermal equilibrium via process (*d*), i.e., go to state *A''A''*; and that of these latter, 90 per cent, or 9 per cent of the total, now return to the *cis* state. Now, increase the frequency of the light to ν' . As before, 9 per cent of the molecules proceed to the *cis* form via the levels *B'B'* and *B''B''*. Of the remaining 90 per cent, a fraction may drop to the *A* level; and many of these will have acquired thermal equilibrium (process *c*), and hence their energy condition will be represented largely by *A''A''* rather than *A'A'*. If 50 per cent follow this path, the total yield of *cis* will be over 50 per cent; i.e.,

$$.09 + .50 \times .90 = 54 \text{ per cent}$$

Olson's model has been developed more extensively than can be advantageously described here. For further details, the reader is referred to the original papers, as well as to a paper by Mulliken¹⁰ in which the subject is fully considered. However, before dismissing the subject, brief mention must be made of the model for unsymmetrical compounds, such as the cinnamic acids, $\text{C}_6\text{H}_5\text{CH}:\text{CHCOOH}$, or the citraconic and mesaconic acids, $\text{HOOC}-\text{CCH}_3=\text{CH}-\text{COOH}$.

In Fig. 49, consider a molecule absorbing a photon in the state *AA'*. If, at the instant of absorption, the relative position of the two parts corresponds to *A*, the excitation will be to the *BB'* level. On the other hand, if absorption takes place from *A'*, the excited level will be *CC'*. If it then emits a photon at *C*, it may go directly to the *cis* molecule. Thus it is apparent that, in the case of unsymmetrical compounds, the *trans* $\rightarrow$ *cis* transition may occur at low temperatures and low pressures. At higher pressures, the transition *C'* $\rightarrow$ *D* may be due to collisions of the second kind.

¹⁰ Mulliken, *Phys. Rev.*, **41**, 751 (1932).

9.22 Experimental evidence. We may now consider the experimental evidence. Unfortunately, in the cases available to actual investigation, it is difficult to isolate the different effects caused by change in the frequency of the light. In Olson's model, the assumption has been that the absorption takes place at the $C=C$ bond. In most actual cases, there are complications due to the following facts:

(a) Other light absorbing groups (e.g., the $COOH$ group) are present.

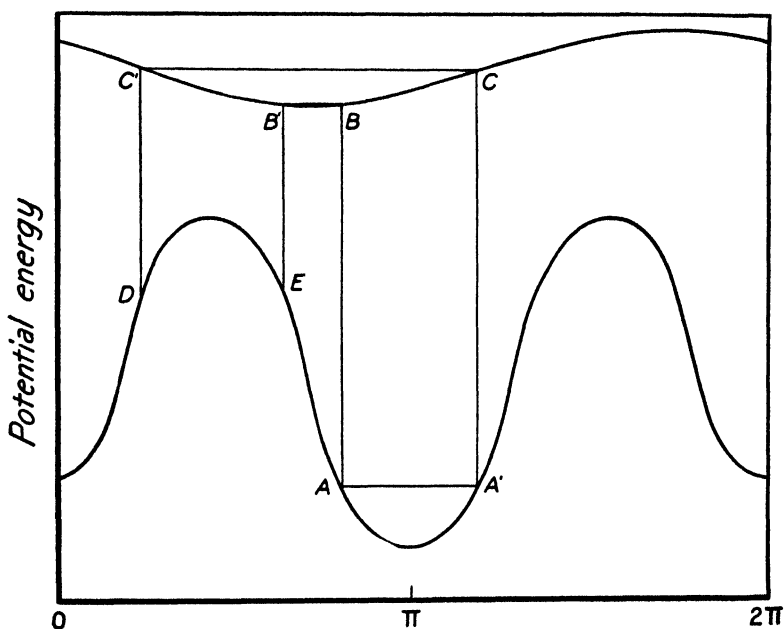


Fig. 49. A Treatment of an Unsymmetrical Molecule.

(b) In many cases the $C=C$ bond in which we are interested may be conjugated with one or more double bonds (e.g., the various acids discussed below, stilbene, etc.).

(c) The *cis* and *trans* forms may not have equal extinction coefficients for the wave lengths employed. This statement probably applies generally.

In consequence we are unable to state definitely the

significance of the finding of Kailan¹¹ that in a fumaric-maleic acid, (*trans-cis*) $\text{HOOCCH}=\text{CHCOOH}$ mixture, the stationary state (75 per cent maleic acid) is roughly independent of wave length. On the other hand, the results of Smakula,¹² who found that the quantum efficiency of conversion of *trans*-stilbene $\text{C}_6\text{H}_5\text{CH}=\text{CHC}_6\text{H}_5$ to the *cis* form in hexane solution decreased steadily from 1.01 at 3130 Å to 0.36 at 1930 Å, are in line with the hypothesis that at the lower wave lengths the phenyl radicals are largely responsible for the absorption. It is interesting to note that, in this case, the complication due to unequal absorptions by the *cis* and *trans* forms is eliminated by the fact that the former decomposes, without rearrangement, to yield unidentified products. Clearly there is some fundamental difference between these two compounds other than the mere factor of orientation; perhaps it is in the type or degree of conjugation, although the similarity in form of the absorption spectra makes this seem unlikely.

The effect of concentration on the quantum efficiency of isomerization of aqueous fumaric and maleic acids is in agreement with Olson's model. The results as measured by Warburg¹³ and by Vaidya¹⁴ are summarized in Table 18. In the case of fumaric acid (*trans*), increase of concentration appears to increase the quantum yield, whereas for maleic acid, the inverse relationship holds. This is in agreement with the finding of Kailan⁹ that at increased concentration the percentage of maleic acid in the photostationary state is also slightly increased.

Data for the two cinnamic acids are also given in Table 18. Olson^{4a} has shown that an increase in the size of the substituted group (in the symmetrical compounds) produces a larger amplitude of oscillation in the excited state and therefore increases the yield. The high quantum efficiency in the case of cinnamic acid, as compared with fumaric

¹¹ Kailan, *Z. physik. Chem.* **87**, 333 (1914).

¹² Smakula, *Z. physik. Chem.*, **B25**, 90 (1934). For more recent results, cf. Lewis, Magel, and Lipkin, *J. Amer. Chem. Soc.*, **62**, 2973 (1940).

¹³ Warburg, *Sitzb. preuss. Akad. Wiss., Physik-math. Klasse*, **33**, 960 (1919).

¹⁴ Vaidya, *Proc. Roy. Soc. (London)*, **A129**, 299 (1930).

acid, may be traceable in part to such an effect. However, in order to explain the actual value, 0.61 at 3130 Å, it is necessary to modify the model slightly and to assume a different shape for the upper potential energy level in Fig. 47. This subject has been taken up in detail by Mulliken¹⁰ and by Olson and Hudson.^{4b}

TABLE 18
QUANTUM EFFICIENCIES OF ISOMERIZATIONS

Acid	Concentration <i>m</i>	WAVE LENGTHS				Reference
		3130 Å	2820 Å	2530 Å	2070 Å	
		QUANTUM EFFICIENCIES				
Fumaric (<i>trans</i>)	0.0102		0.133	0.098	0.104	(1)
	.01	0.118				(2)
	.005	.083				(2)
	.00306		.10	.087	.08	(1)
Maleic (<i>cis</i>)	.00102		.032	.043	.032	(1)
	.01	.048				(2)
	.00514		.035	.049	.037	(1)
	.005	.0525				(2)
Cinnamic (<i>trans</i>)	.003	.61				(2)
Isocinnamic (<i>cis</i>)	.003	.206				(2)

REFERENCES

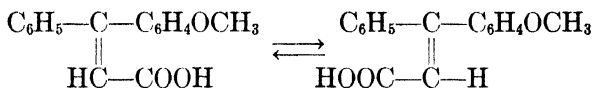
- (1) Warburg, *Sitzb. preuss. Akad. Wiss., Physik.-math. Klasse*, **33**, 960 (1919).
- (2) Vaidya, *Proc. Roy. Soc. (London)*, **A129**, 299 (1930).

The latter have measured the photostationary states at various temperatures for several acids: fumaric-maleic and citraconic-mesaconic (*cis-trans*), at ~ 3341 – 2967 Å; and cinnamic-isocinnamic, at ~ 3130 and 2537 Å. Similar measurements were made by Olson and Maroney^{4d} on the dichloroethylenes¹⁵ and dibromoethylenes. In none

¹⁵ An attempt by Mahncke and Noyes, *J. Am. Chem. Soc.*, **58**, 932 (1936), to study the isomerization of $(\text{CHCl})_2$ in the range 1980–1860 Å was unsuccessful, since both the *cis* and *trans* forms polymerize at those wave lengths.

of this work was it practicable to use monochromatic light. Consequently there was some difficulty in interpretation of the results in the photostationary state. In a general sort of way, it may be said that the *cis/trans* ratio exceeded 1.0 and fell off with increase in temperature, as might be expected from the model. The results with the cinnamic acids, however, were contrary to what might be expected on the basis of the simple model, and require further explanation.

Many other *cis-trans* reactions are photosensitive. Among those that have been investigated in varying degree are the *ortho*-hydroxyphenyl bromoethylenes,¹⁶ the dibenzoylthylenes¹⁷ and the *ortho*-anisylcinnamic acids.¹⁸ The latter gives an equimolal mixture of *cis* and *trans* isomers in the quartz ultraviolet on 160 to 200 hours exposure, according to the reaction



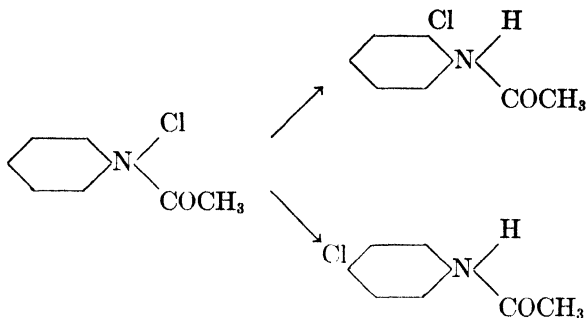
In the case of the dibenzoylthylenes, the reaction goes quantitatively to the labile *cis* form.

9.3 Interchange of two atoms within a molecule. The concept of a direct interchange between two atoms in the same molecule has been advanced by some investigators. Very little work has been done on this type of rearrangement. The principal compounds studied have been acetylchloroaminobenzene (N-chloroacetanilide) and benzoylchloroaminobenzene. On suitable chemical or photochemical treatment, the former rearranges to give the *ortho* and *para* chloroacetanilides as shown on the following page:

¹⁶ Stoermer and Simon, *Ber.*, **37**, 4163 (1904).

¹⁷ Paal and Schulze, *ibid.*, **35**, 168 (1902).

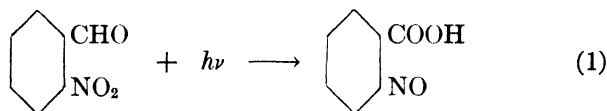
¹⁸ Stoermer, *ibid.*, **42**, 4865 (1909).



and the latter behaves analogously. However, the results are such as to indicate that, in aqueous solution at any rate,¹⁹ even in the photochemical case,²⁰ a simple interchange does not occur but that an intermediate reaction is required.

On the other hand, that a direct interchange actually can take place seems to be supported by the work of Porter and Wilbur,²¹ on dry crystals of the former in the light of the quartz mercury arc; and by Chattaway and Orton,²² on crystals of the latter. In both cases, the compounds slowly rearrange as indicated above. However, shift of atoms between adjacent molecules is an equally good mechanism to explain the effects observed, even in the case of the solids.

9.4 Shift within a molecule. *Ortho*-nitrobenzaldehyde rearranges on illumination with light of $\leq 4360 \text{ \AA}$ to give *ortho*-nitrosobenzoic acid:²³



with no side or reverse reactions. Analogous reactions occur

¹⁹ Cf. Barnes and Porter, *J. Am. Chem. Soc.*, **52**, 2973 (1930); Olson, Porter, Long, and Halford, *ibid.*, **58**, 2467 (1936); Olson, Halford, and Hornel, *ibid.*, **59**, 1613 (1937).

²⁰ Cf. Porter, *Molecular Rearrangements*, Reinhold Publishing Corp., New York, 1928, p. 75.

²¹ Porter and Wilbur, *J. Am. Chem. Soc.*, **49**, 2145 (1927).

²² Chattaway and Orton, *J. Chem. Soc.*, **75**, 1053 (1899).

²³ Ciamician and Silber, *Ber.*, **34**, 2040 (1901).

for 2,4-dinitrobenzaldehyde and 2,4,6-trinitrobenzaldehyde.²⁴

The quantum efficiency for the mono-nitro compound is almost exactly one-half.²⁵ The investigations have been extended by Leighton and Lucy.²⁶ Their results are summarized in Table 19. It is notable that at longer wave lengths, except for the tri-nitro compound in solution, the quantum efficiencies cluster about 0.5, falling off in the solid

TABLE 19
QUANTUM EFFICIENCIES OF ISOMERIZATION OF THE
NITRO-BENZALDEHYDES

Substance	Solvent ^a	Concentration %	Wave Length Å	γ
Ortho.	Acetone	0.03	4040	0.46
	Acetone	.5	3660	.51
	Ligroin	.04	3660	.52
			3660	.50
			3130	.51
			2654	<.5
2,4	Acetone	.5	3660	.49
	Acetone	.1	3660	.48
	Acetone	.01	3660	.48
			3660	.51
			3130	.26
			2654	.12
2,4,6	Acetone	.5	3660	.66
	Acetone	.1	3660	.66
	Ligroin	.04	3660	.17
			3660	.50
			3130	.17
			2654	.06

^a When a solvent is not indicated, the reference is to the solid state.

²⁴ Cohn and Friedländer, *Ber.*, **35**, 1265 (1902); Sachs and Kempf, *ibid.*, **35**, 2704 (1902).

²⁵ Weigert and Kummerer, *Ber.*, **46**, 1207 (1913); Weigert and Brodinan, *Z. physik. chem.*, **120**, 24 (1926); Weigert and Pruckner, *ibid.*, Bodenstein-Festband, 775 (1931). Cf. Bowen, Hartley, Scott, and Watts, *J. Chem. Soc.*, **125**, 1218 (1924); Zimmer, *Z. physik. Chem.*, **B23**, 239 (1933); Wegscheider, *Monatsh.*, **62**, 101 (1933).

²⁶ Leighton and Lucy, *J. Chem. Phys.*, **2**, 756 (1934); Lucy and Leighton, *ibid.*, **2**, 760 (1934).

state with decrease of wave length. In the case of the 2,4,6 compound, the efficiency is somewhat higher in acetone solution and considerably lower in ligroin.

The quantum mechanical model set up by Lucy and Leighton to explain these results may be described qualitatively by the statement that they have taken into account the effect of rotation and orientation, of the CHO and NO₂ groups concerned, on the probability of dissipation of the absorbed energy by energy transfer, by deactivation, and by reaction. In brief, it may be said that the energy is absorbed in either one of the NO bonds in the NO₂ group, and that only one of them is in good position for movement of the O atom *into* the C—H bond of the CHO group. Deactivation by the remainder of the molecule or by surrounding (solvent) molecules may occur before such transfer can take place, thus decreasing the yield in the favorably orientated bond below unity. On the other hand, when absorption takes place in the unfavorably orientated bond, there is a possibility that the NO₂ group may rotate into a favorable position, or that the energy may be transferred to the favorably orientated bond before dissipation of energy can occur. In this way absorption in an unfavorable bond actually results in a yield greater than zero. Lucy and Leighton have shown that the mean of the two effects is ~ 0.5 . The high results with the 2,4,6 compound are explained merely by a peculiarly favorable orientation which promotes freedom of rotation of the nitro group and thus more than compensates for the supposedly unfavorable absorption in the 4-NO₂ group. The lower quantum yield in ligroin may then be ascribed to restriction on the rotation of the NO₂ groups by the solvent, or reduction in the probability of the transfer of the O atom. Similar statements apply to the solid state.

As for the effect of lower wave lengths, it has already been noted (see stilbene, § 9.3) that a decrease in quantum yield at lower wave lengths may result from the fact that other parts of the molecule may be absorbing and dissipating the active light; i.e., the decrease may be attributed to an inner filter effect. Of course, there is also the possibility that the

time required for deactivation (i.e., by a redistribution of the energy within the molecule) may be less at the shorter wave lengths.

Küchler and Patat ²⁷ have found that the quantum yield in the gas phase for *ortho*-nitrobenzaldehyde is 0.75 at 90° and a pressure of 4 mm. On addition of 700 mm. of nitrogen, the yield drops to 0.5. According to the model of Lucy and Leighton, the high efficiency in the gas phase at low pressures would be due to decreased probability of deactivation by collisions of the second kind. The effect of the nitrogen is merely to increase that probability. The model is admittedly incomplete. Nevertheless it is a good qualitative picture to explain the observations.

In the discussion of the ketones (§ 8.76), mention has been made of the opinion of Glazebrook and Pearson ²⁸ that isopropyl radicals formed in the photolysis of isopropyl ketone apparently rearrange on reaction with the metal mirror to yield the normal radical. This case is cited because it is apparently an extremely simple illustration of the shift of a hydrogen atom from one carbon atom to the next member of the chain with an energy of activation which is probably very low. Certainly it does not seem more improbable than a shift from one molecule to another, such as is assumed for the disproportionation reaction of ethyl radicals. The idea is by no means foreign to chemical ideas; we are acquainted with a similar shift in the case of *keto-enol* tautomerism. Perhaps the intermediate formation of a hydrogen bond is involved. There is no need to think of it as the sudden popping over of a proton from one position to the other; the transition may be quite gradual.

However, as to the actual illustration cited, it must be emphasized that the evidence is not conclusive. The radicals resulting from both normal and isopropyl ketones have approximately the same half-lives, and the products ultimately isolated from reactions of those radicals are always the normal propyl compounds. There is thus the

²⁷ Küchler and Patat, *Z. Elektrochem.*, **42**, 529 (1936).

²⁸ Glazebrook and Pearson, *J. Chem. Soc.*, 1777 (1936).

possibility that the reaction may take place in the vapor phase



However, the similarity of half-lives may be wholly fortuitous, and the rearrangement responsible for the production of normal propyl compounds may occur in the wall reaction. In such a case, reaction (2) would not be an illustration of a simple shift within a molecule.

9.5 Other reactions. The preceding discussions have been restricted to those cases where emphasis has been placed on the study of mechanisms. Other photochemical rearrangements have, of course, been made. The reader is referred to the original literature for a series of studies of the *o*-nitrobenzylidene acetals²⁹ and of diazoline derivatives.³⁰

²⁹ Cf. Tanasescu and Ionescu, *Bull. soc. chim.*, [5] **3**, 1517 (1936).

³⁰ Lifschitz and Froentjes, *Rec. trav. chim.*, **55**, 753 (1936).

CHAPTER X

PHOTOSENSITIZATION

10.1 Nature of photosensitization. In order for a photochemical reaction to occur, a certain minimum energy is required; the reactive system must be illuminated by light of corresponding wave length, equal to or shorter than a certain maximum. This maximum wave length may be called the *photochemical threshold*. In some cases the threshold may coincide with the beginning of a continuum or of a predissociation region. To produce a photochemical reaction (e.g., a photolysis) in a substance incapable of absorbing the light used, it is necessary to introduce into the system a substance capable of absorbing that light and conveying the energy so absorbed to the reactants. If this energy is sufficient to cause reaction and if the absorbing substance is not permanently transformed thereby, the process is known as *photosensitization*. The mechanism by which the transfer is effected is immaterial to this definition.

Since the sensitizer is not destroyed in the process, it is evident that a very small amount may be effective, for the individual molecule may go through the same cycle of operations repeatedly. For this reason small amounts, even traces, of the sensitizer may be used. A certain simplicity is introduced into the study of reactions in this way. If neither the reactants nor their products absorb light in the wave-length region used, it is possible to determine the quantum yield of a reaction in an unequivocal manner. Furthermore, in the case of rupture of a simple molecule, it may be possible to set an upper limit for the bond strength lower than can be determined from a study of the pure substance.

Photosensitization is not confined to any state of matter or to any size molecule. Atoms, such as those of mercury,

cadmium, and xenon, are effective. Reactions photosensitized by halogen molecules include decompositions and rearrangements. The uranyl ion sensitizes the photolysis of oxalate ion in aqueous solution. Photo-oxidations and reductions of organic compounds are sensitized by zinc oxide in a heterogeneous process. Chlorophyll sensitizes the photosynthesis of carbohydrates, and dyes have long been used to extend and modify the sensitive range of photographic plates.

In this chapter we are concerned with the essential mechanism of photosensitization. Only the simplest cases are considered here. Some of the others are treated more extensively in later chapters.

10.2 Xenon-sensitized dissociation of hydrogen. The continuum of the absorption spectrum of hydrogen begins at $849.4 \text{ \AA}$.¹ However, the bond strength of the para-hydrogen molecule is only 102.7 kcal. ,² corresponding to a wave length of $\sim 2766 \text{ \AA}$. It thus follows that any wave length less than that value is energetically capable of disrupting the hydrogen molecule, although such a phenomenon is not to be expected in the case of pure hydrogen at wave lengths longer than the beginning of the continuum. Calvert³ has found that, when a trace of xenon is introduced into hydrogen and the mixture is illuminated with the xenon resonance line $1469 \text{ \AA}$, decomposition of the hydrogen occurs. In this case there seems to be no doubt as to the mechanism. The reactions must be:



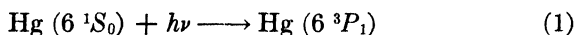
Since a rare gas is involved, there is no reason to consider the possibility of the formation of an intermediate compound. The mechanism of energy transfer is a collision of the second kind, in which the transferred energy raises the molecule to a repulsive state causing dissociation in one vibration period. (Cf. § 3.34.)

¹ Dieke and Hopfield, *Z. Physik*, **40**, 299 (1927); Schaafsma and Dieke, *ibid.*, **55**, 176 (1929).

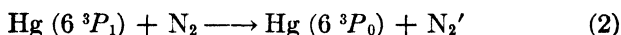
² Table 30 (Appendix II).

³ Calvert, *Z. Physik*, **78**, 479 (1932).

10.3 Mercury-sensitized reactions. The mercury spectrum has two resonance lines, at 2537 and 1850 Å, which are conveniently accessible for photochemical investigation. A simple reaction caused by the former is the sensitized fluorescence of thallium vapor containing a trace of Hg. Many of the phenomena accompanying that reaction, such as the various effects of foreign gases, apply equally well to other photochemical reactions. The initial process is



Such an excited mercury atom may react with thallium vapor, producing an excited (e.g., $7\ ^2S$) Tl atom. Since a considerable number of the excited Hg atoms may lose their energy by fluorescence before a collision with a Tl atom can occur, the yield of excited Tl, and Tl fluorescence, is not high. The yield may be increased by picking off a little of the energy of the excited Hg atom and pocketing the atom, so to speak, in a metastable state. This is accomplished, for example, by the introduction of nitrogen into the mixture. The reaction is



where the nitrogen molecule has acquired extra vibrational energy. Such metastable mercury atoms can gain energy by light absorption but cannot fluoresce. At low pressures, in the absence of energy acceptor particles (e.g., Tl atoms), Hg ($6\ ^3P_0$) atoms have a life of 10^{-3} sec.⁴ They can lose energy only by a collision of the second kind or by reaction; i.e., by just such a process as is characteristic of photosensitization.

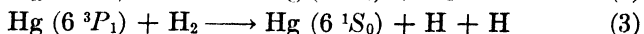
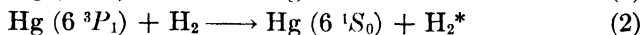
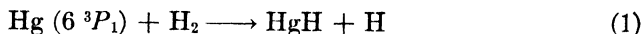
10.31 Mercury-sensitized dissociation of hydrogen. It was discovered by Cario and Franck⁵ that, when a mixture of hydrogen and mercury vapor is illuminated by the 2537 Å resonance line, there is produced an active form of hydrogen which is strongly absorbed on the walls of the container and which is capable of reducing metallic oxides. Senftleben⁶

⁴ Pool, *Phys. Rev.*, **38**, 955 (1931).

⁵ Cario and Franck, *Z. Physik*, **11**, 161 (1922).

⁶ Senftleben, *Z. Physik*, **33**, 871 (1925).

showed that, under these conditions, the gas has an abnormally high thermal conductivity. These properties are characteristic of atomic hydrogen.⁷ Unlike xenon-sensitized decomposition (§ 10.2), there is the possibility of more than one mechanism for the process in this case; three have been postulated:



The energy of excitation of mercury in the $6\ ^3P_1$ state is 112 kcal. All three reactions are energetically permissible. The presence of HgH in these mixtures has been demonstrated by its fluorescence spectrum⁸ (cf. § 3.34). The evidence for reaction (2) is based upon some observations on sensitized water formation (§ 10.32); however, work by Olson and Meyers on sensitized reactions involving ethylene (§ 13.21), as well as some experiments conducted by Storch and Olson⁹ with hydrogen in the low-voltage arc, indicate that the effects observed are properly attributable to the formation of hydrogen atoms rather than excited hydrogen molecules. Indeed, on theoretical grounds,¹⁰ the most probable result of a collision of the second kind is a process involving transformation of a minimum amount of energy into kinetic energy. Since the decomposition of molecular hydrogen into atoms requires ~ 103 kcal., it is evident that reaction (3) would be expected to be favored over the others, just as the experimental results indicate (see, however, § 3.34).

The $6\ ^3P_0$ state of mercury is 107 kcal. above the ground state. That it also is effective in causing decomposition of H_2 has been demonstrated in experiments by Cario and Franck¹¹ and by Meyer.¹² The former studied the quench-

⁷ Langmuir, *J. Am. Chem. Soc.*, **34**, 860 (1912).

⁸ Gaviola and Wood, *Phil. Mag.*, **6**, 1191 (1928); Beutler and Rabinowitch, *Z. physik. Chem.*, **B8**, 403 (1930).

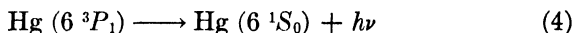
⁹ Storch and Olson, *J. Am. Chem. Soc.*, **45**, 1605 (1923).

¹⁰ Nordheim, *Z. Physik*, **36**, 496 (1926).

¹¹ Cario and Franck, *Z. Physik*, **37**, 61 (1926).

¹² Meyer, *Z. Physik*, **37**, 639 (1926).

ing of fluorescence of mercury vapor by nitrogen and by hydrogen at 18° and at 750°, using at the higher temperature a concentration of mercury vapor corresponding to saturation at 18°. Although hydrogen has the same quenching ability at both temperatures, nitrogen has none at 750°. The explanation is, of course, simple. The hydrogen deactivates the Hg (6^3P_1) atom via reaction (3), and thus prevents the occurrence of the reaction



Nitrogen, however, functions by removing only part of the energy, leaving the mercury atom in the Hg (6^3P_0) metastable state from which fluorescence cannot occur (cf. § 10.3). At the lower temperature the metastable atom quickly loses its activation energy by diffusion to the wall or by collision with a molecule of impurity (e.g., hydrogen, accidentally present). However, at the higher temperature, conditions are somewhat different. The metastable state lies only 0.2 volts or 5 kcal. below the stable state. Before complete deactivation can occur, the metastable atom may acquire sufficient energy, by a collision with a nitrogen molecule in a higher vibrational level, to return to the labile state. Consequently the presence of the nitrogen is without effect on the resonance emission by mercury at high temperatures.

Cario and Franck also showed that at 750° hydrogen quenches the resonance fluorescence of mercury vapor much more efficiently in the presence of nitrogen than when alone. This observation is directly comparable to the mercury-sensitized fluorescence of thallium in the presence of nitrogen (§ 10.3). If a labile (6^3P_1) Hg atom collides with a hydrogen molecule, it is immediately deactivated. If it should collide first with a nitrogen molecule, it is only partially deactivated, yielding the metastable (6^3P_0) atom. The latter in turn may collide with a hydrogen molecule in an inelastic collision, yielding an unexcited Hg atom before a collision of the *first* kind can occur with another nitrogen molecule. In this way, the resonance emission by mercury is effectively decreased.

The results just described and their explanation are in complete consonance with observations of Meyer, which indicate that at ordinary temperatures the quantum yield of the photosensitized decomposition of hydrogen into atoms is increased by the presence of nitrogen. In this case, just as in the case of the sensitized thallium fluorescence, the function of the nitrogen molecule is merely to fix the Hg atom in the 6^3P_0 state until a deactivating collision with a hydrogen molecule can occur. From his results, Meyer calculated that the 6^3P_1 and 6^3P_0 states are practically equally efficient for the production of hydrogen atoms.

Atomic hydrogen is extremely active, readily entering into reactions with metallic oxides and sulfides, oxygen, unsaturated hydrocarbons, nitrous oxide, and carbon monoxide, and to a lesser degree with carbon dioxide. Such atomic hydrogen can be produced by more than one method; namely, from molecular hydrogen at high temperatures and low pressures,⁷ by the passage of a high voltage discharge through moist hydrogen,¹³ and by the method of Cario and Franck just described. Both of the latter two methods have been used extensively. In the following sections we shall concern ourselves principally with the results of those reactions of atomic hydrogen which have been sensitized by mercury vapor.¹⁴

10.32 Reaction between hydrogen and oxygen. The problems presented by this reaction have excited the interest of a multitude of able investigators.¹⁵ Unfortunately, the

¹³ Wood, *Phil. Mag.*, **42**, 729 (1921); **44**, 538 (1922); *Proc. Roy. Soc. (London)*, **A97**, 455 (1921); **A102**, 1 (1922). Cf. Copaux, Perperot, and Hocart, *Bull. soc. chim.*, **37**, 141 (1925).

¹⁴ For a summary of the early work, see H. S. Taylor, *Trans. Faraday Soc.*, **21**, 560 (1926).

¹⁵ (a) For references up to 1934, see Hinshelwood and Williamson, *The Reaction between Hydrogen and Oxygen*, Oxford University Press, 1934. A few papers which have referred rather thoroughly to literature prior to their publication are: (b) Taylor, *J. Am. Chem. Soc.*, **48**, 2840 (1926); (c) Bates and Lavin, *ibid.*, **55**, 81 (1933); (d) Bates and Salley, *ibid.*, **55**, 110 (1933); (e) Kassel and Storch, *ibid.*, **57**, 672 (1935); (f) H. A. Smith and Kistiakowsky, *ibid.*, **57**, 835 (1935); (g) Cook and Bates, *ibid.*, **57**, 1775 (1935); (h) von Elbe and B. Lewis, *ibid.*, **59**, 656 (1937); (i) Rodebush, Wende, and Campbell, *ibid.*, **59**, 1924 (1937). (j) See Norrish and Griffiths, *Proc. Roy. Soc. (London)*, **A139**, 147 (1933), for the reaction sensitized by NO_2 .

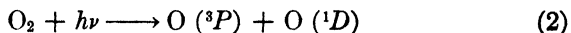
subject is so complicated that, although there is now much information concerning it, our knowledge of the actual mechanisms involved is still very meager. The problem has been approached thermally, electrically, and photochemically.

A disadvantage of the unsensitized photochemical attack lies largely in the fact that, at the wave lengths used, the products found (namely, H_2O , O_3 , and H_2O_2) absorb the light as readily as the original reactants. Smith and Kistiakowsky¹⁵ succeeded in obtaining reaction by illumination in the two regions 1862–1854 Å and 1725–1719 Å. In the first region, excited oxygen molecules are produced by the absorption;¹⁶ in the second, the light dissociates oxygen molecules in one primary act, yielding a normal and an excited atom.¹⁷ In a rough way, the quantum yield of ozone increases with the percentage of oxygen in the mixture, approaching 2.0 as an upper limit (cf. § 12.3, on the formation of ozone); the yield of hydrogen peroxide decreases from a maximum observed value of 0.7 to zero as a lower limit. The yield of water seems to be determined by secondary reactions.

According to Smith and Kistiakowsky, the excited oxygen molecules formed in the long wave length region react with other oxygen molecules



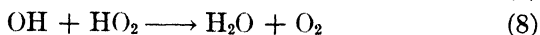
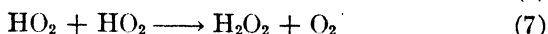
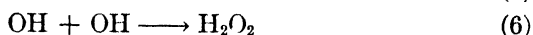
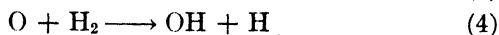
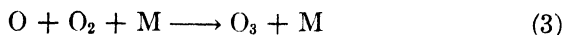
but suffer only elastic collisions with hydrogen molecules, and hence each quantum absorbed produces one ozone molecule and one oxygen atom. Depending on the relative amounts of oxygen and hydrogen present, the O atom then enters into other reactions, which will be the same for both light regions studied. However, in the shorter wave-length regions the absorption process produces two oxygen atoms per quantum absorbed:



¹⁵ Birge and Sponer, *Phys. Rev.*, **28**, 259 (1926).

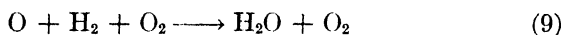
¹⁷ Herzberg, *Z. physik. Chem.*, **B4**, 223 (1929).

and the quantum yields of the secondary products are therefore twice as great in that region as they are in the region of longer wave lengths. Possible reactions appear to be:

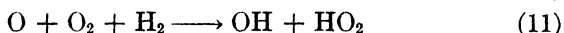
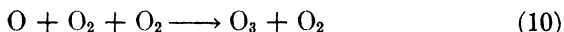


As for the relative probabilities of reactions (3) and (4), Schumacher¹⁸ states that practically every triple collision of an O atom with an O₂ molecule yields ozone, while Harteck and Kopsch¹⁹ report that, at most, only one in 10⁷ collisions with a H₂ molecule is productive.^{19a} At the present time there does not appear to be any support for reaction (6).²⁰ There is no evidence that reaction (5) can go as a two-body collision^{15g} but it does seem possible as a three-body process.

In order to make the mechanism fit their experimental curves more closely, Smith and Kistiakowsky suggested a reaction



and also pointed out that a somewhat arbitrary representation of their data may be arrived at by replacing equations (3), (4), and (5) by



followed by reactions (6), (7), and (8). However, since at the present time it seems necessary to exclude the possibility

¹⁸ Schumacher, *J. Am. Chem. Soc.*, **52**, 2377 (1930); *Z. physik. Chem.*, **B17**, 405, 417 (1932).

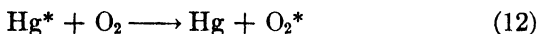
¹⁹ Harteck and Kopsch, *Z. physik. Chem.*, **B12**, 327 (1931).

^{19a} The results of Neujmin and Popov, *Z. physik. Chem.*, **B27**, 15 (1934), with O₂ irradiated below 1750 Å, and of Schumacher, *J. Am. Chem. Soc.*, **52**, 2854 (1930), with NO₂ irradiated at < 2450 Å, indicate that the reaction involving an excited O atom, i.e., O (¹D) + H₂ → OH + H, occurs more readily.

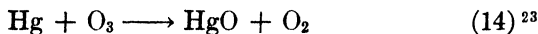
²⁰ Bonhoeffer and Pearson, *Z. physik. Chem.*, **B14**, 1 (1931), studied the electrical discharge through water vapor and observed the emission spectrum of OH. They were unable to isolate H₂O₂ from the products.

of reaction (6) ^{20a} and since even with this assumed mechanism they were unable to account for their results at low pressure, it may be concluded that the problem of the mechanism of the direct photochemical reaction between hydrogen and oxygen is still to be solved.

Aside from the difficulty of interpretation of the results of the direct photochemical method, there is an experimental difficulty which does not encourage workers in this field; namely, the short wave length at which the work has to be done. The mercury-sensitized reaction between hydrogen and oxygen is conducted in a readily accessible region (2537 Å) where the ordinary quartz vessels may be conveniently used. Furthermore, an element of simplicity appears to be introduced by the presumption that there is only one primary reaction; namely, that between H and O₂. Unfortunately, not even this statement is necessarily true. For one thing, it is possible that the molecule HgH (see § 10.31) may play a part in the reaction. In the second place, the excited mercury atom may be deactivated by an oxygen molecule ²¹ by virtue of excitation of O₂ from a ³Σ level to a ¹Σ level, conservation of spin momentum being maintained.²²



The excited oxygen molecules may now undergo several reactions, e.g., reaction (1), thus producing ozone to some extent. There is also the possibility of the reactions



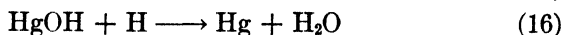
^{20a} At the Stanford University Symposium on the Photochemistry of Polyatomic Molecules (Aug. 9–11, 1938), Teller pointed out that, in order for reaction (6) to occur, the two OH dipoles have to approach each other so as to produce a repulsion. An energy of activation for the reaction is therefore to be expected.

²¹ Evans, *J. Chem. Phys.*, **2**, 726 (1934).

²² Zemansky, *Phys. Rev.*, **36**, 919 (1930), has suggested that the quenching process may be due to the production of mercuric oxide.

²³ Dickinson and Sherrill, *Proc. Nat. Acad. Sci.*, **12**, 175 (1926), observed that the production of ozone was accompanied by the formation of mercuric oxide. Cf. I. M. Frank, *Compt. rend. acad. sci. U.R.S.S.*, (N.S.) **1933**, 146 (in English 147).

Evans ²¹ suggested that there might be successive reactions of HgO so formed and H atoms:

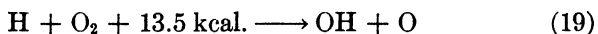


as well as with the HO₂ complex already mentioned. Cf. reaction (5).



Still another complication in the study of the photosensitized reactions must not be ignored. The products may be sensitive both to the radiation used and to excited mercury atoms. It is for this reason that not until flow methods were used was the formation of hydrogen peroxide detected.²⁴ Later Bates and Taylor ²⁵ concluded that hydrogen peroxide is the sole primary product of the photosensitized reaction. This statement was supported by the findings of Bonhoeffer and Böhm,²⁶ who reported 75 per cent H₂O₂ in the products of the reaction of molecular oxygen with hydrogen atoms produced by an electrical discharge. In further work with the mercury-sensitized reaction, Bates and Salley ^{15d} obtained yields of H₂O₂ in excess of 85 per cent.

Several mechanisms have been proposed to explain the various phenomena observed. To begin with, the reaction



appears to be ruled out at ordinary temperatures because of its high energy of activation.²⁷ However, it is a possibility which must be reckoned with in high temperature reactions such as Kassel and Storch ^{15e} and von Elbe and Lewis ^{15h} have discussed. Although there is general agreement among

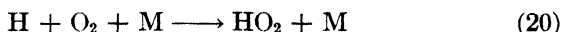
²⁴ Cf. Marshall (a) *J. Phys. Chem.*, **30**, 34, 1078 (1926); (b) *J. Am. Chem. Soc.*, **49**, 2763 (1927); (c) *ibid.*, **54**, 4460 (1932).

²⁵ Bates and Taylor, *J. Am. Chem. Soc.*, **49**, 2438 (1927).

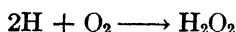
²⁶ Bonhoeffer and Böhm, *Z. physik. Chem.*, **119**, 385 (1926); Bonhoeffer and Löb, *ibid.*, **119**, 474 (1926).

²⁷ See Tables 30 and 31 (Appendix II) for data from which this figure is calculated.

the various investigators²⁸ that, at low temperatures, the first step probably results in the formation of HO₂, there has been dispute as to whether it is by reaction (5) or the corresponding three-body process



From a study of the photochemical oxidation of gaseous hydrogen iodide, Cook and Bates^{15b} concluded, in conformity with a previously expressed opinion of Bodenstein and Schenk,²⁹ that there is no evidence that HO₂ can be formed by a two-body process. The stability of this radical has been indicated by Bray,³⁰ who mentioned in this connection the existence of the stable alkali superoxides. However, a question beyond mere stability is involved in this case. Of the ~ 136 kcal. produced in the reaction



52 kcal. are produced in the addition of the first H atom. The H atom involved in reaction (1) may have an energy of ~ 5 kcal. associated with it because of its method of formation. There is thus a matter of a maximum of ~ 57 kcal. per mole associated with the HO₂ molecule to be stabilized. According to calculations of Kimball,³¹ HO₂ formed in a two-body process should have a mean life of 1.1×10^{-12} sec.; i.e., it should decompose before it can take part in a stabilizing collision.

According to the mechanism proposed by Bates,³² the two steps after the formation of HO₂ are



²⁸ Cf. Taylor, ref. 15b; Marshall, ref. 24; Bonhoeffer and Haber, *Z. physik. Chem.*, **A137**, 263 (1928); *Z. angew. Chem.*, **42**, 475 (1929); Farkas, Haber, and Harteck, *Naturwissenschaften*, **18**, 266 (1930); Frankenburger and Klinkhardt, *Trans. Faraday Soc.*, **27**, 431 (1931).

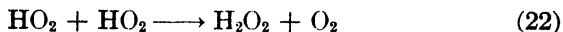
²⁹ Bodenstein and Schenk, *Z. physik. Chem.*, **B20**, 420 (1933); cf. L. Farkas and Sachsse, *ibid.*, **B27**, 111 (1934).

³⁰ Bray, *J. Am. Chem. Soc.*, **60**, 82 (1938).

³¹ Kimball, *J. Chem. Phys.*, **5**, 310 (1937).

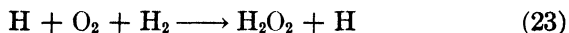
³² Bates, *J. Am. Chem. Soc.*, **55**, 426 (1933); *Proc. Nat. Acad. Sci.*, **19**, 81 (1933); *J. Chem. Phys.*, **1**, 457 (1933); *Chem. Rev.*, **17**, 406 (1935).

^{32a} Reaction (21) has been criticized by Bodenstein and Schenk, *Z. physik. Chem.*, **B20**, 420 (1933), who find it to be contradictory to the observation that O₂ inhibits the H₂ + Cl₂ reaction (cf. § 11.32). However, Kornfeld, *ibid.*, **B35**, 236 (1937), has shown that the formation of one molecule of H₂O₂ would break two chains in that reaction.



The minimum energy of activation required for the first reaction is evidently the difference between the heat of formation of H_2 (~ 103 kcal.) and the heat of addition of the second H atom in H_2O_2 (~ 84 kcal.). Thus we see that the minimum energy of activation of reaction (21) is 19 kcal. While such a figure introduces no problems insofar as high temperature reactions are concerned, it does present an insurmountable obstacle to the reaction at the low temperature of the usual photochemical process, unless the HO_2 can be presumed to have associated with it a quantity of energy in excess of that amount. It was for this reason perhaps that Bates presumed the HO_2 was formed in a two-body process, for in this way the quasi-molecule would have associated with it the ~ 57 kcal. already mentioned. However, it does not seem to us that such a presumption is necessary to Bates' mechanism.

If we consider the three-body process (20), we can see that the energy may be distributed approximately equally between the products HO_2 and M, particularly if the latter is O_2 . Then HO_2 will possess ~ 28.5 kcal. excess energy, an amount insufficient to cause spontaneous dissociation but sufficient, perhaps, to initiate reaction (22). On the other hand, if the third body in reaction (20) is H_2 , the whole process of formation of H_2O_2 may occur in one step:



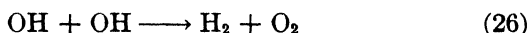
Other mechanisms than that of Bates' have been proposed. The one suggested by Taylor and Marshall does not include reaction (22); the one presented by Haber and his co-workers²⁷ requires the formation of at least 51.4 weight per cent of water as an essential part of the process. In view of the already cited findings of Bates and Salley that the product is over 85 per cent H_2O_2 , such a mechanism is unacceptable. It is interesting that, by his mechanism, Bates was able to reconcile the apparently discordant re-

sults of Marshall ^{24c} and of Frankenburger and Klinkhardt.³³ He showed, by means of kinetic equations, that not only did his mechanism fit the data of the former on the influence of (H₂) and (O₂) on the rates but, in addition, that it explained the fact that working at low light intensities Marshall found a quantum yield of 2.6, whereas at intensities about a hundredfold higher Frankenburger and Klinkhardt obtained a value of ~ 0.8 .

In concluding a discussion of the mechanism of the photosensitized reactions, it is well to mention, first, that Bates himself points out an inability to explain certain low temperature, static experiments of Barak and Taylor,³⁴ and, second, that the complexities suggested by Evans (i.e., involving HgO) are not lightly to be disregarded. Other possible complexities appear from the results of Rodebush, Wende, and Campbell,¹⁵ⁱ working with the reaction occurring in the electrodeless discharge. They indicate, for example, a possible low pressure reaction



Possible reactions of the OH radicals are:



Of course, in the flow experiment, as studied by Bates and Salley,^{15d} reaction (24) and the subsequent ones might not occur. However, as a result of this discussion, it is perhaps apparent why von Elbe and Lewis ^{15h} included nine reactions in their mechanism of the explosive process, and why Kassel and Storch ^{15e} considered fourteen. It may be that further information concerning these reactions, eliminating such complexities as are inherent in the method of photosensitization, can best be obtained by producing H atoms outside the reaction vessel in an electric discharge (cf. § 10.31) and

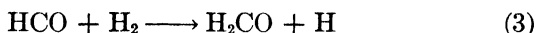
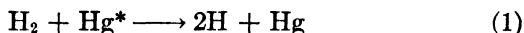
³³ Frankenburger and Klinkhardt, *Z. physik. Chem.*, **B8**, 138 (1930); **B15**, 421 (1932). For quantum yield, cf. R. N. Smith, Leighton, and Leighton, *J. Amer. Chem. Soc.*, **61**, 2399 (1939).

³⁴ Barak and Taylor, *Trans. Faraday Soc.*, **28**, 569 (1932).

introducing them into oxygen in the manner employed so many years ago by Bonhoeffer and his co-workers.^{26, 35}

10.33 Reaction between carbon monoxide and hydrogen.

CO and H₂ react in the presence of excited Hg vapor to yield formaldehyde, solid polymerization products, and some methane.³⁶ In view of the readiness with which hydrogen atoms react with carbon compounds (cf. § 5.5), the formation of the methane is not at all strange. Using methods similar to those he employed in the H₂-O₂ reaction, Marshall³⁷ calculated the quantum yield of HCHO to be 1.7–2.2. Although considerably lower than his first reported value (~ 6), this figure is still somewhat higher than the yield of 1.4 aldehyde groups reported by Frankenburger.³⁸ To explain Marshall's results, the following chain mechanism is required:



On the other hand, Frankenburger showed that glyoxal was produced in amounts commensurate with the formaldehyde. To explain this result, the reactions



are proposed.³⁹ According to the latter mechanism, two HCO groups are formed per H₂ molecule decomposed (i.e., per photon absorbed), but one may be destroyed via reaction (4). Thus the quantum yield must lie somewhere between 1 and 2, depending on the relative probabilities of reactions (4) and (5). As may be expected from the mechanism, the

³⁵ Cf. Geib and Harteck, *Z. physik. Chem.*, **A170**, 1 (1934). Taylor and Salley, *J. Am. Chem. Soc.*, **55**, 96 (1933), studied the reaction between O₂ and H atoms formed in the photolysis of NH₃.

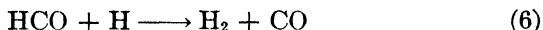
³⁶ Marshall and Taylor, *J. Phys. Chem.*, **29**, 1140 (1925).

³⁷ Marshall, *ibid.*, **30**, 1078, 1634 (1926); cf. Taylor, *Z. physik. Chem.*, **120**, 183 (1926).

³⁸ Frankenburger, *Z. Elektrochem.*, **36**, 757 (1930).

³⁹ Cf. § 8.72 for a discussion of the stability of the HCO radical.

quantum yield is independent of pressure at high pressures. However, at very low pressures the reaction



may assume importance, thus cutting down the yield of HCHO. This reaction explains some experiments of Bonhoeffer and Böhm²⁶ conducted with hydrogen atoms from an electric discharge and therefore at low pressure, in which only very slight formation of HCHO was observed.

10.34 Reaction between carbon dioxide and hydrogen. Bonhoeffer and Böhm²⁶ found that CO₂ and atomic H (from the electric discharge) react to give formaldehyde. Marshall,³⁶ studying the mercury-photosensitized process, found that, although HCHO is formed, the yield of that reaction is only about 2 per cent that of the CO-H₂ reaction (cf. § 10.33) under similar conditions.

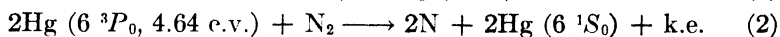
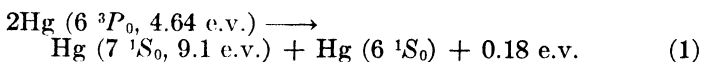
10.35 Reaction between nitrous oxide and hydrogen. According to Marshall,³⁶ N₂O and atomic H formed by mercury sensitization react more rapidly than do O₂ and H under similar conditions. Water is formed, but the reaction is complicated by the fact that the N₂O is itself decomposed by excited Hg atoms.

10.36 Reaction between nitrogen and hydrogen. The possibility of synthesizing ammonia by a reaction between molecular nitrogen and atomic hydrogen has naturally captured the imagination of many workers. However, according to B. Lewis,⁴⁰ who has summarized the results of his own and previous investigations, the evidence indicates that neither atomic hydrogen and molecular nitrogen nor molecular hydrogen and excited nitrogen will react. Excitation of both reactants is required. Since mercury vapor excited to the 6 ³P₁ state does not excite N₂ (cf. § 10.3), synthesis of NH₃ might not be expected. Nevertheless, Noyes^{40a} succeeded in detecting formation of NH₃ at pressures of one atmosphere and higher at the temperature of boiling mercury. The result is explained by Noyes on the

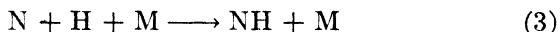
⁴⁰ B. Lewis, *J. Am. Chem. Soc.*, **50**, 27 (1928).

^{40a} Noyes, *ibid.*, **47**, 1003 (1925); **52**, 2418 (1930).

basis of experiments by Gaviola^{40b} and a paper of Beutler and Rabinowitch.^{40c} Gaviola observed the NH absorption band at 3360–3370 Å in a mixture of N₂ and H₂ in the presence of excited Hg, the intensity of the band being proportional to the square of the intensity of the exciting light. The heat of dissociation of N₂ is 169.3 kcal. (cf. Appendix II, Table 30) or 7.3 e.v. Beutler and Rabinowitch suggest that this energy may be obtained from two metastable (6 ³P₀) Hg atoms which may react according to either of the reactions



where the excess 0.18 e.v. in reaction (1) appears as kinetic energy and where the excess in reaction (2) is considerably greater. As there is no doubt of the production of atomic hydrogen under these conditions, the formation of NH₃ may be explained by the reaction



followed by possible reactions with H₂ or three-body collisions with H. Since excited Hg also causes the decomposition of NH₃ (cf. § 10.42) the yield must be low.

10.41 Mercury-sensitized decomposition of water. Senftleben and Rehren⁴¹ have shown that water is decomposed by excited mercury. Using a flow method, Bates and Taylor²⁵ found that the residual gas consists of 73 parts, by volume, of H₂ and 27 parts of O₂. On the other hand, Melville⁴² found in a static experiment that the uncondensable product is exclusively H₂. Judging from the discussion of the reactions of oxygen and hydrogen (§10.32), it is probable that the oxygen deficiency, in the first case, is attributable to the formation of hydrogen peroxide; in the static experiment, Melville's explanation that HgO

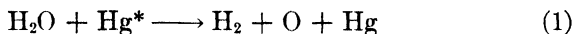
^{40b} Gaviola, *Nature*, **122**, 313 (1928); *Phys. Rev.*, **34**, 1373 (1929).

^{40c} Beutler and Rabinowitch, *Z. physik. Chem.*, **B6**, 233 (1930).

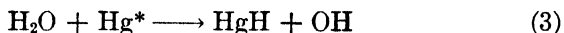
⁴¹ Senftleben and Rehren, *Z. Physik*, **37**, 529 (1926).

⁴² Melville, *Proc. Roy. Soc. (London)*, **157**, 621 (1936).

is a product seems reasonable. We may see from Table 31 (Appendix II) that, although ΔH is ~ 217.7 kcal. for the reaction $\text{H}_2\text{O} \rightarrow 2\text{H} + \text{O}$, it is only ~ 115 kcal. for both the reactions $\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}$ and $\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}$. The excited Hg (6^3P_1) atom supplies 112 kcal. per mole. Thus, both the reactions

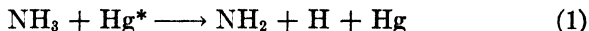


may occur at nearly every collision at ordinary temperatures. (We have seen in § 10.32 that H_2O may be produced by reactions in which the formation of either H or O atoms is a primary process.) On the other hand, the fluorescence experiments of Beutler and Rabinowitch⁴³ indicate that the reaction

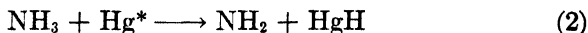


may be the actual primary process.

10.42 Decomposition of ammonia. Experiments on the mercury-photosensitized decomposition of NH_3 were conducted mainly with the idea of elucidating the mechanism of the ordinary photolysis and of determining more precisely the energy required for the primary step.⁴⁴ On the basis of other experiments, it is now fairly well established (cf. § 7.7) that the first step in the decomposition is the formation of an NH_2 radical and a H atom. Since excited Hg (6^3P_1) atoms are sufficient to produce the decomposition, it may consequently be concluded that the strength of the broken $\text{N}-\text{H}$ bond is < 112 kcal. Of course, such an estimate is only a first approximation. In addition to the possible primary process



there may be the alternative reaction



⁴³ Beutler and Rabinowitch, *Z. physik. Chem.*, **B8**, 403 (1930).

⁴⁴ Cf. Dickinson and Mitchell, *Proc. Nat. Acad. Sci.*, **12**, 692 (1926); Taylor and Bates, *ibid.*, **12**, 714 (1926); Mitchell and Dickinson, *J. Am. Chem. Soc.*, **49**, 1478 (1927); Bates and Taylor, *ibid.*, **49**, 2438 (1927); Romeyn and Noyes, *ibid.*, **54**, 4143 (1932).

analogous to a suggested mechanism for the decomposition of H_2 (cf. § 10.31). The heat of formation of HgH is ~ 8 kcal. per mole; it may be concluded that the maximum value for the strength of the broken $N-H$ bond is raised by that amount, i.e., to ~ 120 kcal. On the other hand, reaction (2) probably has an energy of activation. If that energy were known, the maximum strength of the bond might be decreased by that amount.

The sensitized decomposition of ND_3 has also been studied.⁴⁵

10.51 Some other sensitization reactions: determination of activation energies. It is shown in Chapter XI that many reaction chains include intermediate processes in which atoms or radicals are involved. For the complete elucidation of such processes, it is essential to have information concerning the activation energy of such steps. The method of sensitized reactions has provided a frequently used tool for the determination of those energies. The procedure, roughly speaking, is to attempt to isolate the effects of temperature on any processes occurring concurrently and, from such effects, to calculate the activation energies. Naturally, such calculations are sometimes open to criticism, but it is beyond the scope of this book to subject the methods to detailed analysis. Instead, we indicate in Table 33 (Appendix III) a few activation energies and the methods used in their determination, and at the same time append the warning that the reader should examine the original papers carefully to determine from them what their authors consider the limitations of their methods. Estimates of activation energies of a large number of other reactions are to be found in tables compiled by Rice and Rice.⁴⁶

10.52 Sensitized formation of ozone. This subject has been discussed briefly in the section on the reactions between hydrogen and oxygen. The first work appears to have been performed by Dickinson and Sherrill,²³ who saturated

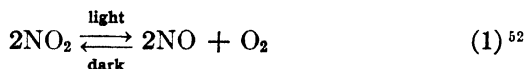
⁴⁵ Jungers and Taylor, *J. Chem. Phys.*, **2**, 373 (1934).

⁴⁶ F. O. Rice and K. K. Rice, *The Aliphatic Free Radicals*, Johns Hopkins Press, Baltimore, 1935.

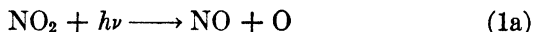
pure oxygen with mercury and passed the resulting gas through an irradiated quartz vessel and thence into KI solution. Subsequently, other experiments were performed by Noyes,⁴⁷ who used a static method. Insight into the processes involved has been afforded in more recent years by study of the sensitized oxygen-hydrogen reactions (§ 10.32).

10.53 Sensitized decomposition of nitrogen pentoxide.

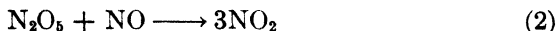
Although ΔH for the reaction $\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + \text{O} (^3P_2)$ is only 61.16 kcal., corresponding to 4660 Å, the longest wave length at which simple photolysis has been observed seems to be 2800 Å (cf. § 7.44). On the other hand, when N_2O_5 is mixed with nitrogen dioxide ($2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$), decomposition occurs on exposure to blue light, $\lambda = 4600\text{--}4000$ Å.⁴⁸ Fazel and Karrer⁴⁹ suggested a mechanism for the process involving the excitation of NO_2 or N_2O_4 , and the transfer of this energy by a collision of the second kind to N_2O_5 , thus causing decomposition. This mechanism, however, is unsupported by experimental evidence. On the other hand, a mechanism proposed by Norrish⁵⁰ is in close agreement with what is known of the reactions and the properties of the substances involved.⁵¹ The steps are:



Alternatively, we may write



Then



Thus the nitrogen dioxide decomposed in the initial step is reformed by the subsequent reaction, and the net effect is simply a decomposition of N_2O_5

⁴⁷ Noyes, *J. Am. Chem. Soc.*, **49**, 3100 (1927).

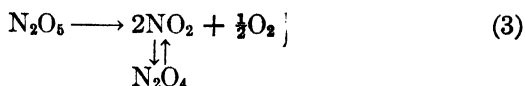
⁴⁸ Daniels and Johnston, *J. Am. Chem. Soc.*, **43**, 72 (1921).

⁴⁹ Fazel and Karrer, *ibid.*, **48**, 2837 (1926).

⁵⁰ Norrish, *Nature*, **119**, 123 (1927).

⁵¹ Cf. Holmes and Daniels, *J. Am. Chem. Soc.*, **56**, 630 (1934).

⁵² See § 7.43 for a discussion of this reaction.



The nitrogen dioxide may be regarded as the photosensitizer.

Some other photosensitized decompositions are indicated in Table 20.

TABLE 20
SOME PHOTOSENSITIZED DECOMPOSITIONS

Substance	Primary Step	Reference
HN_3	$\text{Hg}^* + \text{HN}_3 \rightarrow \text{Hg} + \text{N}_2 + \text{HN}$	(1)
AsH_3	$\text{Hg}^* + \text{AsH}_3 \rightarrow \text{AsH}_2 + \text{H} + \text{Hg}$	(2)
CH_4	$\text{Hg}^* + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} + \text{Hg}$	(3)
CH_3OH		(4)
$\text{C}_2\text{H}_5\text{OH}$		(4)
C_6H_{14}		(4)
C_6H_6	$\text{Hg}^* + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5 + \text{H} + \text{Hg}$	(4)
HCOOH		(4)
$\text{C}_2\text{H}_5\text{NH}_2$		(4)
C_6H_{14}	$\text{NH}_3^* + \text{C}_6\text{H}_{14} \rightarrow \text{C}_6\text{H}_{13} + \text{H} + \text{NH}_3$	(5)
C_2H_6	$\text{Hg}^* + \text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3 + \text{Hg}$	(6)

REFERENCES

- (1) Myers and Beckman, *J. Am. Chem. Soc.*, **57**, 89 (1935).
- (2) Simmons and Beckman, *ibid.*, **58**, 454 (1936).
- (3) Morikawa, Benedict, and Taylor, *J. Chem. Phys.*, **5**, 212 (1937).
- (4) Taylor and Bates, *Proc. Nat. Acad. Sci.*, **12**, 714 (1926).
- (5) L. Farkas, *Z. physik. Chem.*, **B23**, 89 (1933).
- (6) Steacie and Phillips, *J. Chem. Phys.*, **6**, 179 (1938).

10.6 Reactions photosensitized by the halogens. A number of reactions are known, in the gas phase and in solution, in which the photosensitizer is a halogen. Usually the sensitized reaction is accompanied by another which involves the halogen, but the latter can often be made negligible as compared to the main reaction. The primary effect of the absorption of a light quantum is the dissociation of the halogen molecules.⁵³ The halogen atoms then enter into a series of reactions which, in the case of sensitized

⁵³ Evidence for this step is presented in § 4.2 for the regions of continuous absorption, and in § 4.5 for the band region. Additional evidence is presented in Chapters XI and XII.

reactions, ultimately bring about the reformation of halogen molecules and certain changes in the composition of the reaction mixture. In a number of systems the sensitized reaction is so closely correlated with a reaction involving the halogen and one of the reactants that it is advantageous to discuss the two simultaneously. Reference is therefore made to later sections for the following chlorine-sensitized reactions: formation of water (§ 11.33); formation of carbon dioxide (§ 11.4); and the oxidations of methane (§ 11.5), chloroform (§ 11.5), and tetrachloroethylene (§ 12.42).

10.61 Chlorine-sensitized decomposition of ozone. In 1907 Weigert⁵⁴ reported that, if mixtures of chlorine and ozone are illuminated by violet light, the ozone is decomposed with no net change in the chlorine. He reported the rate of the reaction to be proportional to the light absorbed by the chlorine and independent of the ozone concentration between very wide limits. Bonhoeffer⁵⁵ confirmed these results and added the statement that, for wave lengths between 4060 and 4360 Å, two molecules of ozone are decomposed per quantum absorbed. Later investigations, however, have shown that the behavior of this system is much more complicated than was indicated in the first reports. Allmand and Spinks⁵⁶ found quantum yields as high as 59. Bodenstein, Harteck, and Padelt⁵⁷ found that exposure of a bulb filled with chlorine and ozone to sunlight causes the formation of a red oil of the empirical composition ClO_3 . This observation was confirmed by Norrish and Neville,⁵⁸ and by Byrns and Rollefson,⁵⁹ using blue light. The latter also demonstrated that considerable quantities of Cl_2O_7 are formed in the reaction mixture.

Rollefson and Byrns⁶⁰ also showed that ClO_3 reacts thermally with ozone in such a manner that the net change

⁵⁴ Weigert, *Ann. Physik*, **24**, 243 (1907).

⁵⁵ Bonhoeffer, *Z. Physik*, **13**, 94 (1923).

⁵⁶ Allmand and Spinks, *J. Chem. Soc.*, 599 (1932).

⁵⁷ Bodenstein, Harteck, and Padelt, *Z. anorg. allgem. Chem.*, **147**, 233 (1925).

⁵⁸ Norrish and Neville, *Nature*, **131**, 544 (1933).

⁵⁹ Byrns and Rollefson, *J. Am. Chem. Soc.*, **56**, 2245 (1934).

⁶⁰ Rollefson and Byrns, *ibid.*, **56**, 364 (1934).

in the system is principally the decomposition of ozone. The rate of this reaction was found to be given by the equation

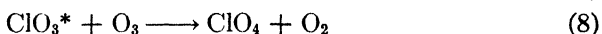
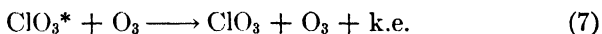
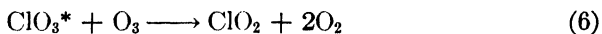
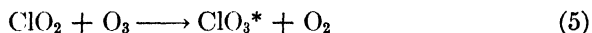
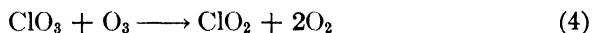
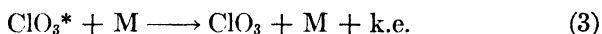
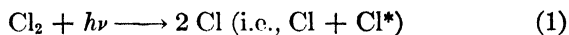
$$-\frac{d(O_3)}{dt} = \frac{k(ClO_3)(O_3)}{1 + k_1 \frac{(M)}{(O_3)}} \quad 10-1$$

in which (M) represents the concentration of any gases, such as oxygen, nitrogen, etc. In systems originally containing only ClO_3 and ozone, M is O_2 . The heat of activation corresponding to k is ~ 11 kcal.

It is apparent that the curve obtained by plotting change of pressure against time for illuminated mixtures of chlorine and ozone is the resultant of the effects due to several reactions rather than a measure of the rate of disappearance of ozone, as was assumed at first. Furthermore, the use of the term *quantum yield* is of no significance, since, as soon as some ClO_3 is formed, a thermal reaction is initiated which will continue after the light is shut off. Under such conditions there is no finite limit to the value of the *apparent* quantum yield. The rate of disappearance of the ozone depends to a considerable extent on the pressure of ClO_3 built up in the system and on the rate of formation of this oxide. Rollefson and Byrns found that, in order to account for the observed facts in the thermal reaction between oxide and ozone, it was necessary to assume two forms of this oxide possessing different reactivities, the newly formed molecule being more reactive than those which have been in the system for some time. It was suggested that the more reactive form might have a peroxide structure.

This assumption is useful also in explaining the behavior of illuminated mixtures of chlorine and ozone. Byrns and Rollefson⁵⁹ found that the rate of disappearance of ozone in such mixtures is greater than can be accounted for solely by the thermal reaction between the ozone and the ClO_3 . Under the experimental conditions such a discrepancy is to be expected; because of their formation from ozone and the chlorine atoms produced by the light absorption, the

concentration of the more reactive molecules is particularly high. Although the problems involved in this system cannot be said to be completely solved, the information now available is in accord with the following series of reactions:



where k.e. is kinetic energy.

Repetition of reactions (5) and (6) gives a chain mechanism which permits many molecules of ozone to react for each quantum absorbed. M is any molecule which has a deactivating influence on ClO_3^* . Reactions (8) and (9) account for the formation of Cl_2O_7 . Bowen, Moelwyn-Hughes, and Hinshelwood⁶¹ studied the rate of decomposition of ozone in the presence of chlorine in carbon tetrachloride solutions. They report that the rates in the gas phase and in solution are nearly the same and give for the quantum yield a value $\gamma = 2$ at $\lambda = 3660 \text{ \AA}$. The solution reaction almost certainly involves the same complications as the gas phase reaction and requires further study.

10.62 Bromine-sensitized decomposition of ozone. This reaction was reported by Bonhoeffer⁵⁶ to have a quantum yield of 30. It has not been subjected to as extensive study as the chlorine-ozone system, probably because of the existence of a dark reaction. Lewis and Schumacher⁶² studied this dark reaction and reported that it proceeds as a

⁶¹ Bowen, Moelwyn-Hughes, and Hinshelwood, *Proc. Roy. Soc. (London)*, **A134**, 211 (1931).

⁶² B. Lewis and Schumacher, *Z. physik. Chem.*, **B6**, 423 (1930).

chain initiated by the formation of an oxide of bromine on the walls of the reaction vessel. They gave the empirical formula of the oxide as Br_3O_8 . It is probable that any photochemical reaction in mixtures of bromine and ozone is at least as complex as has been found with chlorine.

10.63 Bromine-sensitized rearrangement of maleic acid and its esters into the fumaric compounds. The transformation of maleic acid and its esters into the fumaric compounds occurs in the presence of bromine if the system is illuminated with light in the frequency range absorbed by the bromine molecule. The reverse reaction does not occur. The rearrangement of the free acid was studied by Bruner and Krolikowski.⁶³

A more detailed study with particular emphasis on the reactions of the esters has been carried out by Eggert and his students.⁶⁴ They say that, in order to avoid complications, their experiments were performed with the pure compounds and in carbon tetrachloride solution. The complications referred to are probably dark reactions such as the addition of bromine, which has been studied for aqueous solutions of the acids by Berthoud and Mosset.⁶⁵ Although in carbon tetrachloride, the rearrangement of the esters is always accompanied by some addition of bromine to form dibromosuccinic esters, only the rearrangement has been observed for the acid. The principal experimental results have been summarized by Eggert and are shown in Table 21 (p. 290).

In the table, the notations γ_r and γ_a refer to the quantum yields of the rearrangement and addition reactions respectively. The light intensity was varied sixfold, and the bromine concentration from 0.03 *N* to 0.3 *N*. The ester concentration was varied from pure ester to one mole of ester per 70 moles of CCl_4 .

One of the most puzzling features of the experimental data is the reported change in the quantum yields with wave

⁶³ Bruner and Krolikowski, *Anz. Krakau Akad. Wiss.*, Reihe A, 192 (1910).

⁶⁴ (a) Borinski, Dissertation, Berlin, 1923; Eggert, *Physik. Z.*, **25**, 19 (1924). (b) Wachholtz, *Z. physik. Chem.*, **125**, 1 (1927). (c) Schmidt, *ibid.*, **B1**, 205 (1928); summarized by Eggert, *Z. Elektrochem.*, **33**, 542 (1927).

⁶⁵ Berthoud and Mosset, *J. chim. phys.*, **33**, 272 (1936).

length. Bonhoeffer and Harteck ⁶⁶ have suggested that the lower yield at longer wave length may be attributable to a low efficiency of the primary dissociation process in that region. If this were the correct explanation, the effect should be the same for both the rearrangement and the addition, and also for the acid and its esters. That is not the situation as shown by the facts presented in Table 21.

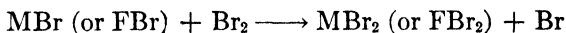
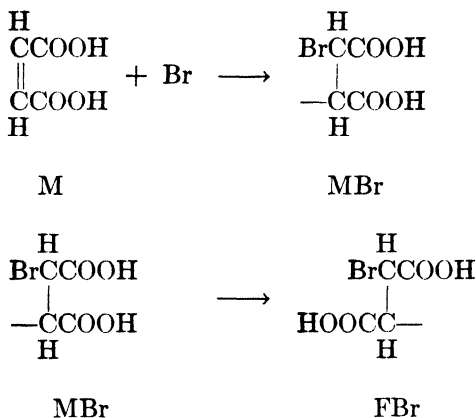
TABLE 21
BROMINE-SENSITIZED PHOTOCHEMICAL REACTIONS OF
MALEIC ACID AND ITS ESTERS

Experimental Conditions	Ethyl Ester	Methyl Ester		Acid
21°C., $\lambda = 4360 \text{ \AA}$, 0.1 N Br ₂ .	$\gamma_r = 295$, $\gamma_a = 8$	$\gamma_r = 430$, $\gamma_a = 11$.		$\gamma_r = 430$.
Light intensity varied.	No effect on either γ_r or γ_a .	High concentration.	Low concentration.	Same as methyl ester.
Concentration of ester varied.	No effect on either γ_r or γ_a .	Same as ethyl ester.	γ_r and γ_a decrease as the concentration of the ester decreases and as the light intensity increases.	
T varied.		γ_r and γ_a both markedly dependent on temperature.		
(Br ₂) varied.		γ_r independent of (Br ₂); γ_a proportional to (Br ₂).		
Effect of Change of λ	Ethyl Ester	Methyl Ester		Acid
$\left. \begin{array}{l} g = 5470 \text{ \AA} \\ b = 4360 \text{ \AA} \\ u = 3650 \text{ \AA} \end{array} \right\}$	$\frac{\gamma_{rb}}{\gamma_{ra}} = 1.9$ $\frac{\gamma_{ab}}{\gamma_{ag}} = 2$	$\frac{\gamma_{rb}}{\gamma_{ra}} = 2.3$ $\frac{\gamma_{ab}}{\gamma_{ag}} = 1.9$		$\gamma_u : \gamma_b : \gamma_g = 5 : 4 : 1$

⁶⁶ Bonhoeffer and Harteck, *Grundlagen der Photochemie*, Theodor Steinkopff, Dresden, 1933, p. 273.

The temperature effect is very marked. Wachholtz ^{64b} reported that, for the ethyl ester, γ_r doubles if the temperature is raised from 19.5° to 23.5°C. For the addition reaction, γ_a doubles between 17° and 25°C.

A mechanism has been presented by Wachholtz which is in qualitative agreement with most of the facts but which involves some *ad hoc* assumptions. The essential feature of the mechanism is the formation of an intermediate by the addition of a bromine atom to a molecule of the maleic compound. This intermediate may rearrange to the fumaric form and then liberate a bromine atom, or it may react with molecular bromine to give the addition product and a bromine atom. These steps can be represented by the following equations:



Wachholtz considered that MBr existed in two forms. One form was a reactive quasi-molecule; the other an inactive molecule, the formation of which constituted a chain-terminating step. The competition between the addition and rearrangement reactions accounts for the dependence of γ_a on the bromine concentration. In order to test this or any other mechanism adequately, it is necessary to secure additional information, particularly with reference to: (1) change of γ with wave length; (2) factors which affect the

chain length; (3) factors which affect the ratio of the rearrangement and addition reactions.

10.64 Bromine-sensitized oxidation of CCl_3Br . Grüss⁶⁷ reported that illumination of a solution of bromine and CCl_3Br in CCl_4 in the presence of air caused an oxidation of the CCl_3Br to COCl_2 , Br_2 , and Cl_2 . He followed the reaction by measuring the increase in light absorption which he attributed to bromine, and he reported the quantum yield as unity. It has been shown that bromine and chlorine react to form BrCl , and under his experimental conditions the reaction would be fairly complete.⁶⁸ The absorption of BrCl is very much less than that of Br_2 at the wave lengths used in the analysis; therefore the actual quantum yield was considerably greater than Grüss reported. The available data indicate that the quantum yield is actually about 10.

10.65 Chlorine-sensitized decomposition of chlorine monoxide. The decomposition of chlorine monoxide into chlorine and oxygen is photosensitive (cf. § 7.52), and this sensitivity can be increased by the presence of chlorine. According to Bodenstein and Kistiakowsky,^{68a} the reaction proceeds with a quantum yield of 2, whether the light is absorbed by Cl_2O or by Cl_2 . The presence of ClO_2 during the course of the reaction was demonstrated by spectroscopic tests. The mechanism which they proposed assumed that the absorption of light produces an activated molecule which reacts with other molecules. That mechanism is not compatible with the evidence now available that chlorine is dissociated by light. A more probable mechanism starts with the dissociation of a chlorine molecule into atoms, or a Cl_2O molecule into Cl and ClO . The data are not sufficient to specify the remaining steps, but provision must be made for the formation of ClO_2 , which itself undergoes a sensitized decomposition. (Cf. § 10.66.)

10.66 Sensitized decomposition of ClO_2 . Chlorine dioxide mixed with either bromine or chlorine is decomposed

⁶⁷ Grüss, *Z. Elektrochem.*, **29**, 144 (1923).

⁶⁸ Vesper and Rollefson, *J. Am. Chem. Soc.*, **56**, 620 (1934).

^{68a} Bodenstein and Kistiakowsky, *Z. physik. Chem.*, **116**, 371 (1925).

when illuminated with light absorbed by the free halogen. The bromine-sensitized reaction has been studied in the gas phase by Spinks and Porter,⁶⁹ and in carbon tetrachloride solution by Spinks and Taube.⁷⁰ There is no great difference between the reactions in the gas phase and in solution. The following facts are listed:

- (1) The quantum yield γ is 0.2 to 0.3.
- (2) γ is independent of the ClO_2 concentration.
- (3) γ decreases with increasing light intensity and with increasing bromine concentration.
- (4) The rate of decomposition approaches dependence on $I_{\text{abs}}^{1/2}$.
- (5) Large amounts of Cl_2O_6 (or ClO_3 in the gas phase) and some Cl_2O appear to be formed.

Spinks and Taube express a preference for a mechanism involving activated bromine molecules. However, in view of the strong evidence from other sources that the bromine is dissociated, some mechanism starting with the atoms must be found. The system is rather complex and requires further work before a satisfactory mechanism can be set up.

The chlorine-sensitized reaction is mentioned by Spinks and Taube, but no detailed study has been published.

10.67 Iodine-sensitized decomposition of ethylene iodide. Polissar⁷¹ showed that the rate of the thermal decomposition of ethylene iodide into ethylene and iodine is given by

$$-\frac{d(\text{C}_2\text{H}_4\text{I}_2)}{dt} = k(\text{C}_2\text{H}_4\text{I}_2)(\text{I}_2)^{1/2} \quad 10-2$$

This law is accounted for by a mechanism in which it is assumed that the decomposition is catalyzed by iodine atoms formed by the thermal dissociation of the iodine present in the system. Schumacher and Wiig⁷² studied the photochemical reaction in carbon tetrachloride solution and found that the rate is given by

$$-\frac{d(\text{C}_2\text{H}_4\text{I}_2)}{dt} = k'(\text{C}_2\text{H}_4\text{I}_2)I_{\text{abs}}^{1/2} \quad 10-3$$

⁶⁹ Spinks and J. M. Porter, *J. Am. Chem. Soc.*, **56**, 264 (1934).

⁷⁰ Spinks and Taube, *Can. J. Research*, **B15**, 499 (1937).

⁷¹ Polissar, *J. Am. Chem. Soc.*, **52**, 956 (1930).

⁷² Schumacher and Wiig, *Z. physik. Chem.*, **B11**, 45 (1930).

This is exactly the form to be expected, since the concentration of the iodine atoms in these solutions is proportional to the square root of the light absorbed. The quantum yield was found to be about 25, under their experimental conditions.

Schumacher and Stieger⁷³ studied the quantum yield at various wave lengths at 99.2° to 99.4°C., and reported that the yield was only one-sixth as great in the region of banded absorption as in the continuum. However, Dickinson and Nies⁷⁴ pointed out that Schumacher and Stieger neglected to take into consideration the fact that the quantum yield is a function of the absorbed light intensity. Taking this fact into consideration, they showed that there is no significant difference in the efficiency of dissociation of the iodine by light of various wave lengths ranging from 4358 to 5790 Å at 76.6° and 99°C.

Polissar also found that the reverse reaction (i.e., the addition of iodine to ethylene) is of importance at lower temperatures and is catalyzed by iodine atoms. This reaction has not been studied in detail photochemically, although it is to be expected that it would occur as an iodine-sensitized reaction on illumination with any wave length which will dissociate iodine. DeRight and Wiig⁷⁵ reported the photochemical addition on illumination with light of $\lambda = 7000 \text{ Å}$. Although there is no direct evidence that such light dissociates iodine, the work of Rabinowitch and Wood⁷⁶ suggests such a possibility. It is unlikely that an activated molecule of iodine would have a sufficiently long life in solution to react with ethylene.

10.68 Iodine-sensitized rearrangement of allocinnamylidenacetic acid. Ghosh, Murthi, and Das Gupta⁷⁷ found that iodine sensitizes the transformation of allocinnamylidenacetic acid, $\text{C}_6\text{H}_5\text{CH}:\text{CH}\cdot\text{CH}:\text{CHCOOH}$, into the normal compound in benzene and carbon tetrachloride

⁷³ Schumacher and Stieger, *Z. physik. Chem.*, **B12**, 348 (1931).

⁷⁴ Dickinson and Nies, *J. Am. Chem. Soc.*, **57**, 2382 (1935).

⁷⁵ DeRight and Wiig, *J. Am. Chem. Soc.*, **58**, 693 (1936).

⁷⁶ Rabinowitch and Wood, *Trans. Faraday Soc.*, **32**, 547 (1936).

⁷⁷ Ghosh, Murthi, and Das Gupta, *Z. physik. Chem.*, **B26**, 255 (1934).

solutions. The rate depends on $I_{abs}^{1/2}$, a fact which is readily accounted for by assuming that the reaction chains are started by $I_2 + h\nu \rightarrow 2I$ and terminated by the recombination $I + I + M \rightarrow I_2 + M$. The quantum yields ranged from 150 to 400 in most of the experiments.

CHAPTER XI

TYPICAL CHAIN REACTIONS

11.1 Definition. The term *chain reaction* may be defined in a number of ways. In one sense, any reaction which proceeds by way of two or more consecutive steps may be called a chain reaction. It is more common to apply the term to reactions that proceed according to a mechanism in which certain steps may be repeated an indefinite number of times. In such systems, a reactive intermediate X is formed in the primary step and initiates a series of reactions in which it is ultimately reformed. The series is repeated until X is removed by some other reaction. Substitution and addition reactions are particularly apt to follow a mechanism of this type.

11.2 Photosynthesis of hydrogen bromide. The most completely studied reaction which proceeds by a chain mechanism is that of hydrogen and bromine to form hydrogen bromide. The reaction chains are very short in this system on account of the fact that the speed of the chain-terminating reaction is greater than that of the chain-continuing one at ordinary temperatures. In fact it is only above 200°C. that the quantum yield is more than two molecules of hydrogen bromide formed for each quantum absorbed.

The rate of the photochemical reaction was studied by Bodenstein and Lütkemeyer¹ at temperatures from 160° to 218°C. According to them, at any one temperature the rate is given by

$$\frac{d(\text{HBr})}{dt} = \frac{k(\text{H}_2)I_{abs}^{1/2}}{1 + k' \frac{(\text{HBr})}{(\text{Br}_2)}}$$

¹ Bodenstein and Lütkemeyer, *Z. physik. Chem.*, **114**, 208 (1925).

Since the quantum yield is the rate divided by I_{abs}

$$\gamma = \frac{k(\text{H}_2)}{I_{abs}^{1/2} \left(1 + k' \frac{(\text{HBr})}{(\text{Br}_2)} \right)}$$

The variation of γ with temperature, for a given value of I_{abs} , is determined by the changes in the constants k and k' . More recent work by several investigators ² has shown that these equations must be modified by the introduction of a factor proportional to the total pressure. The revised equations are:

$$\frac{d(\text{HBr})}{dt} = \frac{k(\text{H}_2)I_{abs}^{1/2}}{p^{1/2} \left(1 + k' \frac{(\text{HBr})}{(\text{Br}_2)} \right)} \quad 11-1$$

$$\gamma = \frac{k(\text{H}_2)}{p^{1/2} I_{abs}^{1/2} \left(1 + k' \frac{(\text{HBr})}{(\text{Br}_2)} \right)} \quad 11-2$$

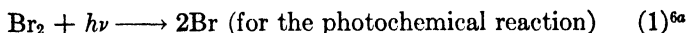
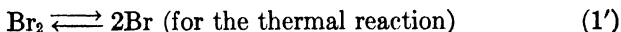
where p represents the total pressure.

The rate equation is closely correlated with the one found by Bodenstein and Lind ³ for the *thermal* reaction between 200° and 300°C.:

$$\frac{d(\text{HBr})}{dt} = \frac{k_T(\text{H}_2)(\text{Br}_2)^{1/2}}{1 + k' \frac{(\text{HBr})}{(\text{Br}_2)}} \quad 11-3$$

The subscripts T designate the values obtained from thermal reaction.

A mechanism which accounts for both the photochemical and the thermal rate laws was proposed independently by Christiansen, ⁴ by Herzfeld, ⁵ and by Polanyi. ⁶ The steps are:



² (a) Jost and Jung, *Z. physik. Chem.*, **B3**, 83 (1929); (b) Ritchie, *Proc. Roy. Soc. (London)*, **A146**, 828 (1934); (c) Hilferding and Steiner, *Z. physik. Chem.*, **B30**, 399 (1935).

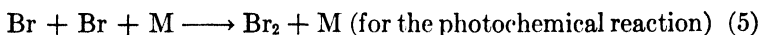
³ Bodenstein and Lind, *Z. physik. Chem.*, **57**, 168 (1907).

⁴ Christiansen, *Dansk. Vid. Math. Phys. Med.*, **1**, 14 (1919).

⁵ Herzfeld, *Z. Elektrochem.*, **25**, 301 (1919).

⁶ Polanyi, *ibid.*, **26**, 49 (1920).

^{6a} Cf. § 4.2.



Reactions (2), (3), and (4) do not cause any net change in the concentration of bromine atoms. For every bromine atom used in reaction (2), one is formed by reaction (3) or (4). Reaction (5) does not need to be considered specifically in the thermal mechanism, because in the equilibrium (1') the law of microscopic reversibility requires that, if the recombination is affected by a third body M, the dissociation must be affected to the same extent (i.e., the equilibrium cannot be shifted by the addition of another substance).

The rate of formation of HBr is given by the sum of the rates of reactions (2) and (3) less that of (4):⁷

$$\frac{d(\text{HBr})}{dt} = k_2(\text{Br})(\text{H}_2) + k_3(\text{H})(\text{Br}_2) - k_4(\text{H})(\text{HBr}) \quad 11-4$$

In order to meet the stoichiometric requirements of the overall equation, as many hydrogen atoms must be produced by reaction (2) as are used by reactions (3) and (4); therefore

$$k_2(\text{Br})(\text{H}_2) = k_3(\text{H})(\text{Br}_2) + k_4(\text{H})(\text{HBr}) \quad 11-5$$

Substituting 11-5 in 11-4,

$$\frac{d(\text{HBr})}{dt} = 2k_3(\text{H})(\text{Br}_2)$$

But from 11-5,

$$(\text{H}) = \frac{k_2(\text{Br})(\text{H}_2)}{k_3(\text{Br}_2) + k_4(\text{HBr})}$$

Therefore

$$\frac{d(\text{HBr})}{dt} = \frac{2k_2k_3(\text{Br}_2)(\text{Br})(\text{H}_2)}{k_3(\text{Br}_2) + k_4(\text{HBr})} \quad 11-6$$

- If the thermal reaction is under consideration, the concentration of bromine atoms is determined by the thermal equilibrium (1') and is equal to $K^{1/2}(\text{Br}_2)^{1/2}$, in which K

⁷ In equation 11-4 and in all other equations, the subscript on the rate constant is the number of the corresponding equation in the mechanism.

is the equilibrium constant. Substituting this value for $(\text{Br})'$ in 11-6 and dividing numerator and denominator by $k_3(\text{Br}_2)$, we obtain

$$\frac{d(\text{HBr})}{dt} = \frac{2k_2K^{1/2}(\text{Br}_2)^{1/2}(\text{H}_2)}{1 + \frac{k_4(\text{HBr})}{k_3(\text{Br}_2)}} \quad 11-7$$

which is identical with 11-3 if we replace $2k_2K^{1/2}$ by k_T and k_4/k_3 by k'_T . In the photochemical reaction the concentration of bromine atoms is determined by reactions (1) and (5) if it is assumed that the thermal concentration is negligible as compared to that produced photochemically. Since as many atoms disappear according to reaction (5) as are formed by reaction (1),

$$2I_{abs} = k_5(\text{Br})^2(p)$$

$$(\text{Br}) = \sqrt{\frac{2I_{abs}}{k_5p}}$$

Substituting this value for (Br) in 11-6 and dividing numerator and denominator by $k_3(\text{Br}_2)$, the photochemical rate is

$$\frac{d(\text{HBr})}{dt} = \frac{2k_2(\text{H}_2)\sqrt{\frac{2I_{abs}}{k_5p}}}{1 + \frac{k_4(\text{HBr})}{k_3(\text{Br}_2)}} \quad 11-8$$

This equation is identical with 11-1 if we write $k = 2k_2\sqrt{2/k_5}$ and $k' = k_4/k_3$. It is apparent that this mechanism requires k' and k'_T to be equal, which is actually the case. Bodenstein and Jung⁸ give 1/8.4 as the best value for $k' = k'_T = k_4/k_3$.

The effect of total pressure on the photochemical reaction was demonstrated by Jost and Jung,^{2a} and has been studied in considerable detail by Ritchie^{2b} and by Hilferding and Steiner.^{2c} The latter investigators were particularly concerned with the efficiencies of various molecules as the third body in reaction (5). The results have been listed in a previous section (§ 5.5). Ritchie also carried out experiments

⁸ Bodenstein and Jung, *Z. physik. Chem.*, **121**, 127 (1926).

at such pressures that the bromine atoms were removed by the walls rather than by reaction (5). Under such conditions the addition of an inert gas accelerates the reaction because of the decreased rate of diffusion to the walls. The order of effectiveness found by Ritchie is $\text{CCl}_4 > \text{CO}_2 > \text{N}_2$ and $\text{O}_2 > \text{A} > \text{H}_2$ and He.

The fact that both the thermal and the photochemical reactions proceed by the same mechanism makes it possible to determine the absolute value of the constants k_2 and k_5 in addition to the ratio k_4/k_3 . The rate of the thermal reaction at the temperatures prevailing in the photochemical experiments can be obtained by a slight extrapolation of the data of Bodenstein and Lind.³ By division of 11-8 by 11-7, we obtain

$$\left(\frac{d(\text{HBr})}{dt}\right)_P / \left(\frac{d(\text{HBr})}{dt}\right)_T = \left(\frac{2I_{abs}}{K(\text{Br}_2) \cdot k_5 p}\right)^{1/2} \quad 11-9$$

The subscripts P and T are used to designate the photochemical and thermal rates respectively. All of the quantities in equation 11-9 except k_5 are capable of direct measurement. The ratio k_4/k_3 is obtained from a study of the retarding effect of HBr. After k_5 and k_4/k_3 have been evaluated, k_2 is readily obtained from any of the rate measurements. According to Bodenstein and Lütkemeyer, k_2 is given by

$$\log k_2 = -\frac{3859}{T} + 13.862$$

where T is the absolute temperature. The corresponding activation energy is 17.64 kcal., which is approximately the same as the heat absorbed in reaction (2). It follows that reaction (4), which is the reverse of (2), must have little or no heat of activation. The ratio k_4/k_3 is independent of temperature; consequently, reactions (3) and (4) have the same heat of activation, both probably being zero. The difference in the rates of these two reactions must be caused partially by a difference in collision number due to differences in the diameters of the Br_2 and HBr molecules, and partially by a requirement of a more specific direction of approach for reaction (4) than for (3).

The reaction was studied at several wave lengths by Jost and Jung.^{2a} They reported no appreciable difference between the reaction initiated by absorption in the band region and that caused by the continuous absorption. This result is in accord with the work of Kondratjew and Polak,⁹ in which the occurrence of induced predissociation in bromine vapor was demonstrated. Similar results have been obtained in the study of other reactions, such as the bromination of acetylene (cf. § 12.44) and the reaction of bromine with platinum.¹⁰

Urmston and Badger studied the latter reaction by illuminating bromine vapor over finely divided solid platinum. At low pressures some fluorescence was detected photographically when light absorbed in the band region was used. If the exciting light was confined to a narrow beam, the fluorescence was limited to the illuminated region. The rate of the reaction with the platinum was independent of the distance between the illuminated zone and the platinum at all wave lengths. Since any activated molecules which are formed do not survive long enough to move an appreciable distance outside the illuminated zone, it follows that some other active form (presumably atoms) must be formed even by the band absorption. It is possible that some of this dissociation may correspond to a continuum underlying the bands, but it may also be a case of induced predissociation (cf. § 4.31). At pressures such as have been used in the study of the hydrogen-bromine reaction, the dissociation is favored to such an extent that it is reasonable to conclude the formation of hydrogen bromide occurs through the atomic chain mechanism under all conditions. The low quantum yield at low temperatures is caused by the high heat of activation of reaction (2), which permits the recombination reaction (5) to remove most of the bromine atoms.

11.21 Addition of thermal and photochemical rates.
Since both the thermal formation and the photochemical

⁹ Kondratjew and Polak, *Z. Physik*, **76**, 386 (1932).

¹⁰ Urmston and Badger, *J. Am. Chem. Soc.*, **56**, 343 (1934).

formation of hydrogen bromide proceed through the same mechanism, it is possible to apply this mechanism to conditions such that both the thermal and photochemical rates are appreciable. From a consideration of reactions (1'), (1), and (5), it is readily shown that the concentration of bromine atoms is

$$(\text{Br}) = \sqrt{K(\text{Br}_2) + \frac{2I_{\text{abs}}}{k_5 p}}$$

The total rate is given by

$$\frac{d(\text{HBr})}{dt} = \frac{2k_2(\text{H}_2)\sqrt{K(\text{Br}_2) + \frac{2I_{\text{abs}}}{k_5 p}}}{1 + \frac{k_4(\text{HBr})}{k_3(\text{Br}_2)}}$$

It is obvious that this equation is not the simple sum of 11-7 and 11-8. The rather common practice of correcting photochemical rates for a dark reaction by subtracting the thermal rate from the total rate is generally unsound. It is even possible for such "corrected" rates to be less accurate than if no correction were made. No strictly valid correction can be made unless the mechanisms of both the thermal and the photochemical reactions are known.

11.3 Photosynthesis of hydrogen chloride. The photochemical reaction of chlorine with hydrogen to form hydrogen chloride has been studied more frequently (but not more completely) than any other photochemical reaction. This reaction has an extremely high quantum yield;¹¹ the highest value reported is 10^6 . Impurities have a marked effect and are responsible for the extreme variations in the experimental results which have been reported. A complete survey of the literature on this subject would be more confusing than helpful. Our discussion will be limited to a presentation of the most recent information on the reaction in mixtures of pure hydrogen and chlorine, and the effect of adding other substances (particularly oxygen, which causes water formation).

¹¹ Bodenstein and Winter, *Sitz. Preuss. Akad. Wiss., Physik.-math. Klasse*, 1 (1936).

11.31 Reaction in pure hydrogen and chlorine. Practically all of the early work on this reaction was carried out with reaction mixtures that were not completely free from oxygen. Recently several investigators have published results on the oxygen-free mixtures.¹² All agree that the rate of the reaction is proportional to the hydrogen pressure. Bodenstein and Unger^{12a} give the rate law as

$$\frac{d(\text{HCl})}{dt} = kI_{\text{abs}}(\text{H}_2)$$

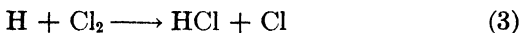
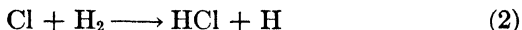
This law also represents the data of Bodenstein and Winter,¹¹ and of Potts and Rollefson,^{12c} except that the experiments of the latter showed a slight systematic trend which was attributed to an inhibiting action by HCl analogous to that found for HBr in the hydrogen-bromine reaction. Ritchie and Norrish^{12b} reported a much more complex rate law, in which the exponent of I_{abs} was less than unity and allowance was made for a large inhibiting action by HCl. For reasons which will be presented in connection with the discussion of the mechanism of the reaction, their work must be considered as affected by some unknown impurity which introduced unnecessary complications into the rate law.

Craggs and Allmand^{12e} found that the exponent of I_{abs} varied from 0.5 to 1.0, depending on the experimental conditions. They also found a retarding effect of chlorine at relatively high pressures. Their results are not expressed in terms of a rate law; rather, they considered the effect which changes in the experimental conditions had on the exponents of (Cl_2) and I_{abs} in a rate equation. The hydrogen pressures were always of the order of 0.1 mm. or less, and the chlorine pressure ranged from 0.012 to 450 mm. At high chlorine pressures and high light intensities, the rate depends on $I_{\text{abs}}^{1/2}$; at low chlorine pressures the rate gradually changes to a dependence on I_{abs} . At constant light

¹² (a) Bodenstein and Unger, *Z. physik. Chem.*, **B11**, 253 (1930); (b) Ritchie and Norrish, *Proc. Roy. Soc. (London)*, **A140**, 112 (1933); (c) Potts and Rollefson, *J. Am. Chem. Soc.*, **57**, 1027 (1935); (d) Bodenstein and Winter, *loc. cit.*; (e) Craggs and Allmand, *J. Chem. Soc.*, 241 (1936); (f) Squire and Allmand, *ibid.*, 1869 (1937).

intensity, variation of the chlorine pressure causes the quantum yield to pass through a maximum. Their results were obtained at much higher $(\text{Cl}_2)/(\text{H}_2)$ ratios than were used in any other experiments.^{12a,c,d} This fact appears to be the reason for the apparently different results.

The simple rate law given by Bodenstein and Unger can be deduced from an atomic chain mechanism first proposed by Nernst.¹³ The steps are:



Since every hydrogen atom formed by reaction (2) reacts according to (3), the rate of formation of HCl is twice the rate of (2); i.e.,

$$\frac{d(\text{HCl})}{dt} = 2k_2(\text{Cl})(\text{H}_2)$$

The number of chains started must be equal to the number of chains terminated; therefore

$$2I_{\text{abs}} = k_4(\text{Cl})$$

$$(\text{Cl}) = \frac{2I_{\text{abs}}}{k_4}$$

Substituting this value in the rate equation, we obtain

$$\frac{d(\text{HCl})}{dt} = \frac{4k_2}{k_4} I_{\text{abs}}(\text{H}_2) \quad 11-10$$

The value of k_2 has been determined by Rodebush and Klingelhoefer,¹⁵ who used chlorine atoms from an electric discharge. Their value corresponds to a heat of activation of 6 kcal. If it is assumed that equation 11-10 is correct

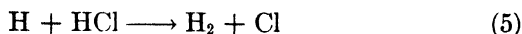
¹³ Nernst, *Z. Elektrochem.*, **22**, 62 (1916).

¹⁴ One of the chlorine atoms produced by the dissociation of a chlorine molecule by light absorbed in the continuum is activated to the $^2P_{1/2}$ state (cf. § 4.2). In this and most other reactions, no effects are observed which can be attributed to the fact that such an atom behaves differently from one in the $^2P_{3/2}$ state. Therefore we shall not indicate any distinction in writing equations.

¹⁵ Rodebush and Klingelhoefer, *J. Am. Chem. Soc.*, **55**, 130 (1933).

and that reaction (4) requires no heat of activation, the heat of activation for reaction (2) may be determined from the temperature coefficient of the overall rate. Such experiments have been performed by Hertel,¹⁶ and by Potts and Rollefson.^{12c} The result is in agreement with that of Rodebush and Klingelhofer.

An inhibiting action by HCl can be accounted for by a reaction analogous to that found for HBr in the hydrogen-bromine reaction



Consideration of this reaction changes 11-10 to

$$\frac{d(\text{HCl})}{dt} = \frac{4k_2}{k_4} \cdot \frac{I_{abs}(\text{H}_2)}{1 + \frac{k_5(\text{HCl})}{k_3(\text{Cl}_2)}} \quad 11-11$$

According to Ritchie and Norrish, the ratio k_5/k_3 is 1.7. This value is not in accord with other data (cf. ref.^{12a,c,d}). An exact value for k_3 is not known, but experiments by Böhm and Bonhoeffer¹⁷ show that reaction (3) occurs at least once in 10^4 collisions. Bodenstein and Schenk¹⁸ estimate that one in 21 collisions is effective, and give the activation energy as 1.9 kcal. The value for k_5 can be calculated from k_2 and the equilibrium constant for reaction (2).^{12c} It corresponds to a collision efficiency of one in 10^5 . Therefore the maximum value that k_5/k_3 can have is 0.1, and it is probably somewhat smaller. The larger retardation reported by Ritchie and Norrish must be due to an impurity introduced with the HCl.¹⁹

The change in the exponent of I_{abs} and also the retarding effect of chlorine at high $(\text{Cl}_2)/(\text{H}_2)$ ratios have been discussed by Craggs, Squire, and Allmand.^{19a} A transition

¹⁶ Hertel, *Z. physik. Chem.*, **B15**, 325 (1932).

¹⁷ Böhm and Bonhoeffer, *Z. physik. Chem.*, **119**, 385 (1926).

¹⁸ Bodenstein and Schenk, *Z. physik. Chem.*, **B20**, 420 (1933).

¹⁹ Potts and Rollefson, working under conditions similar to those used by Ritchie and Norrish, obtained approximately the same effect but were able to show that it was caused by some change introduced by allowing the HCl to stand in a glass vessel.

^{19a} Craggs, Squire, and Allmand, *J. Chem. Soc.*, 1878 (1937).

from I_{abs} to $I_{abs}^{1/2}$ corresponds to a change from reaction (4) as a chain-terminating step to a reaction involving two intermediates, either or both of which may be chlorine atoms. Such a possibility does not arise at moderate pressures of chlorine and hydrogen; a concentration of chlorine atoms sufficient to make the rate of the homogeneous recombination equal to the rate of light absorption would make the rate of formation of HCl too fast to measure by ordinary methods. In the experiments with very low hydrogen pressures, it is possible for the chlorine atom concentration to attain such a magnitude.

Craggs, Squire, and Allmand introduce the additional intermediate Cl_3 to explain their results. In the mechanism they replace reaction (4) by the equilibrium



and the chain terminating step



The rate law deduced from this revised mechanism is

$$\frac{d(\text{HCl})}{dt} = \frac{4k_2}{K_6 k_7^{1/2}} \cdot \frac{(\text{H}_2)I_{abs}^{1/2}}{(\text{Cl}_2)} \quad 11-12$$

This equation gives the required dependence of the rate on the hydrogen and chlorine pressures and on I_{abs} . From their data they calculate the equilibrium constant k_6 to be 0.00491 mm.^{-1} . This value is somewhat lower than the one calculated by Rollefson and Eyring²⁰ by means of quantum mechanics and the assumption that, for reaction (6), the entropy change is -6 . The agreement is well within the limits of error of the calculation. Squire and Allmand reported that the rate law at high chlorine pressures apparently depends on $(\text{Cl}_2)^{-2}$. The additional effect (over that given by 11-12) was shown to be caused by a diffusion of chlorine atoms from the main reaction zone.

The status of the formation of hydrogen chloride in

²⁰ Rollefson and Eyring, *J. Am. Chem. Soc.*, **54**, 170 (1932).

mixtures of pure hydrogen and chlorine may be summarized by the following statements:

(1) At moderate or comparable pressures of both gases, the mechanism of the reaction may be represented by reactions (1) to (5).

(2) At high chlorine pressure and very low hydrogen pressure, reaction (4) is replaced by the equilibrium (6) and (7).

11.32 Effect of impurities on the reaction between hydrogen and chlorine. The formation of hydrogen chloride shows a characteristic common to all chain reactions; namely, a very marked retardation by impurities. It was shown by Burgess and Chapman ²¹ that the induction period (i.e., the initial period during which the reaction proceeds at much less than its maximum rate) is caused by impurities, especially ammonia or other nitrogenous substances. This induction period had been observed in all of the earlier rate measurements. If the effect is due to impurities in the chlorine, it may be eliminated by preilluminating that gas. On the other hand, if the effect is caused by impurities in the reaction vessel, these may be destroyed by running some "clean-up" reactions in which the impurities are destroyed. This procedure is usually applied in the study of chain reactions. The decrease in the retarding action during the course of the reaction is due to the elimination of the inhibitor by a photochemical reaction.

Chapman and MacMahon ²² showed that NO, NH₃, NH₄Cl, and O₂ all act as inhibitors. The decreased rate is the result of chains being broken by the removal of either chlorine atoms or hydrogen atoms. This fact was demonstrated very clearly by experiments of Weigert and Kellerman.²³ By illumination of mixtures of hydrogen and chlorine with a spark, they showed that the reaction continues for some hundredths of a second after illumination ceases. The duration of this after-effect is closely parallel to

²¹ Burgess and Chapman, *J. Chem. Soc.*, **89**, 2, 1399 (1906).

²² Chapman and MacMahon, *ibid.*, **95**, 1717 (1908); **97**, 845 (1910).

²³ Weigert and Kellerman, *Z. physik. Chem.*, **107**, 1 (1923).

the sensitivity of the mixture. The higher the observed quantum yield (i.e., the longer the chains), the longer the time that the reaction continues after the light is shut off.

At one time it was reported that extremely dry mixtures of hydrogen and chlorine would not react on illumination with visible or near-ultraviolet light.²⁴ Several later investigations have shown that such an effect does not exist.²⁵ Craggs and Allmand report a slight retardation by water; the effect is attributed to an acceleration of removal of chlorine atoms by the walls. This is in accord with observations of Rodebush and Klingelhofer.¹⁵

11.33 Effect of oxygen on the hydrogen-chlorine reaction: the chlorine-sensitized formation of water. Bunsen and Roscoe²⁶ were the first to note a retarding action of oxygen on the formation of hydrogen chloride. Weigert²⁷ found that, if a mixture of two volumes of hydrogen, one of chlorine, and one of oxygen is illuminated with light absorbed by the chlorine, about 40 per cent of the hydrogen is converted into water. Bodenstein and Dux²⁸ found that the rate of formation of HCl in the presence of oxygen and with constant light intensity is given by

$$\frac{d(\text{HCl})}{dt} = \frac{k(\text{Cl}_2)^2}{(\text{O}_2)} \quad 11-13$$

This rate law cannot hold for all conditions, as it calls for an infinite rate at zero oxygen pressure. Many other equations have been proposed. The most recent and complete equation is the one given by Bodenstein and Schenk,²⁹ which is:

$$\frac{d(\text{HCl})}{dt} = I_{abs} \left(\frac{k(\text{Cl}_2)}{(\text{O}_2)} + 1 \right) \frac{(\text{H}_2)}{(\text{H}_2) + 0.1(\text{Cl}_2)} \quad 11-14$$

The rate of formation of water in illuminated mixtures of

²⁴ Coehn and Jung, *Z. physik. Chem.*, **110**, 705 (1924).

²⁵ Craggs and Allmand, *Nature*, **130**, 927 (1932); *J. Chem. Soc.*, 1899 (1937). Bernreuther and Bodenstein, *Sitzb. preuss. Akad. Wiss.*, 333 (1933). Rollefson and Potts, *J. Am. Chem. Soc.*, **55**, 860 (1933).

²⁶ Bunsen and Roscoe, *Pogg. Ann.*, 1855-59, reprinted in Ostwald's *Klassiker*, Nos. 34 and 38 (Leipzig, 1892).

²⁷ Weigert, *Ann. Physik*, **24**, 243 (1907).

²⁸ Bodenstein and Dux, *Z. physik. Chem.*, **85**, 297 (1913).

²⁹ Bodenstein and Schenk, *Z. physik. Chem.*, **B20**, 420 (1933).

chlorine, hydrogen, and oxygen is approximately proportional to the chlorine concentration if the light intensity is constant.^{30,31} Bodenstein and Schenk state that the quantum yield of water formation is approximately constant but shows a trend which may be represented by

$$\gamma_{\text{H}_2\text{O}} = \frac{2(\text{H}_2)}{(\text{H}_2) + 3(\text{Cl}_2)} \quad 11-15$$

These statements are consistent, since the experimental conditions were such that the light absorbed was small and therefore proportional to the chlorine concentration.

The role of oxygen as an inhibitor for the hydrogen chloride formation has been greatly clarified by the experiments of Krauskopf and Rollefson, and of Bodenstein and Schenk. The reaction chains may be broken by removal of either a chlorine or a hydrogen atom.



The HO_2 (cf. § 10.32) or ClO_2 molecules enter into secondary reactions, which result in the formation of stable molecules without regenerating free atoms. If reaction (8) is the principal chain terminating step, it should be possible to suppress the formation of HCl completely by the addition of a large amount of oxygen. On the other hand, if reaction (9) terminates the chain, the ratio of the HCl formed to the water formed must approach a definite limit, since one molecule of HCl must be formed for each hydrogen atom formed. Krauskopf and Rollefson studied this ratio as a function of the ratio of the oxygen and chlorine pressures. They found that, as the ratio $(\text{O}_2)/(\text{Cl}_2)$ increases, a limit of approximately one molecule of water to one of HCl is approached. This limit may be deduced from a consideration of reactions (1), (2), (3), and (9). That mechanism gives:

$$\frac{d(\text{HCl})}{dt} = 2I_{\text{abs}} + \frac{4I_{\text{abs}}k_3(\text{Cl}_2)}{k_9(\text{O}_2)} \quad 11-16$$

³⁰ Cremer, *Z. physik. Chem.*, **128**, 285 (1927).

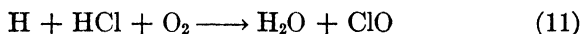
³¹ Krauskopf and Rollefson, *J. Am. Chem. Soc.*, **56**, 327 (1934).

$$\frac{d(\text{H}_2\text{O})}{dt} = 2I_{abs} \quad 11-17$$

$$\frac{d(\text{HCl})}{d(\text{H}_2\text{O})} = 1 + 2 \frac{k_3(\text{Cl}_2)}{k_9(\text{O}_2)} \quad 11-18$$

The more complex equations for $d(\text{HCl})/dt$ and $\gamma_{\text{H}_2\text{O}}$ given by Bodenstein and Schenk are obtained if reaction (8) is added to the mechanism. An inspection of these equations shows that, when the quantum yield for the formation of HCl is moderate or high, 11-16 reduces to the form found by Bodenstein and Dux. The more complex equation of Bodenstein and Schenk reduces to the same limiting form at low chlorine concentrations.

The deductions which have been made from this relatively simple mechanism involve the assumption that, once HO_2 or ClO_2 is formed, the reaction chain is broken and the later reactions of these molecules have no effect on the ultimate result. It is quite possible that this assumption is not always true. For example, if H_2O_2 is formed from the HO_2 , it may react with chlorine to give HCl and O_2 . The chain would still be broken, but the final value of the $\text{HCl}/\text{H}_2\text{O}$ ratio would be affected. It is also possible that some additional reactions must be considered in order to achieve an exact picture of the system under all conditions. Norrish and Ritchie,³² and Krauskopf and Rollefson have found some indications of the reactions



Bodenstein and Schenk have also discussed a number of possibilities which follow the formation of HO_2 . The evidence for all such reactions is qualitative.

11.34 Effect of temperature and of wave length on the rate of formation of hydrogen chloride. The temperature coefficient of this reaction has been studied several times.^{33, 12c, 16} Increase of temperature may affect the rate by

³² Norrish and Ritchie, *Proc. Roy. Soc. (London)*, **A140**, 713 (1933).

³³ (a) Hertel, *Z. physik. Chem.*, **B14**, 443 (1931); **B15**, 325 (1932). (b) Craggs and Allmand, *J. Chem. Soc.*, 241 (1936).

changing the absorption coefficient of the chlorine or by increasing the rates of the reactions in the chain mechanism. It is generally agreed that the temperature coefficient is practically independent of the wave length for any absorption in the continuum. Such small variations as have been observed are caused by change in the light absorption. This result is fully in accord with the mechanism which has been given, since in oxygen-free mixtures the temperature effect is determined by reaction (2). The excess kinetic energy possessed by the atoms formed by absorption of light of high frequencies is of no importance; most of the atoms which enter into reaction (2) are formed by reaction (3).

In the presence of oxygen the temperature effect is much less than for the oxygen-free mixtures. A 10-degree rise in temperature causes the rate to increase by a factor of 1.37 in the latter, and 1.12 in the former.^{33a} The rate equations deduced from the mechanism show that, in the presence of oxygen, the temperature coefficient is determined by the change in the ratio k_3/k_4 .

The effect of light on the long wave length side of the band convergence of chlorine (cf. § 4.2) at $\lambda = 4785 \text{ \AA}$ has been the subject of further discussion. Hertel^{33a} reported that the temperature coefficient in this region is 1.48, as compared to 1.37 in the continuum. He also found, on the addition of inert gases, an increase in the rate which was attributed to the dissociation of activated chlorine molecules on collision. Craggs and Allmand^{33b} reported temperature coefficients of 1.3 at $\lambda = 4360 \text{ \AA}$, and 1.76 at $\lambda = 5460 \text{ \AA}$. Bayliss³⁴ showed that, if correction was made for the change in absorption of the chlorine with temperature, the temperature coefficients were identical at these two wave lengths. The energy of activation for the reaction which follows the absorption of light is therefore independent of the wave length.

No change in quantum yield with change of wave length is to be expected for any absorption in the continuous portion

³⁴ Bayliss, *Trans. Faraday Soc.*, **33**, 1339 (1937).

of the spectrum. In the band region a decrease can be expected, and values have been reported which are 0.3 to 0.5 of that found at shorter wave lengths. Semenoff³⁵ has calculated that, if the reaction in this region is due solely to chains initiated by excited chlorine molecules, the quantum yield should be about 1/9 of that found at shorter wave lengths. Recent work by Jones and Spooner,³⁶ and by Aickin and Bayliss,³⁷ has shown that a continuous absorption accompanies the band absorption to wave lengths much longer than 5000 Å. According to Aickin and Bayliss, this continuum is at least partly due to transitions to the $^3\Pi_{1u}$ state, which dissociates into normal atoms. Some of the reaction occurring at these wave lengths must be due to chains started by atoms. As a matter of fact, Bayliss³⁴ has pointed out that, if it is assumed that only the continuous absorption initiates reaction chains, the quantum yield is independent of wave length even up to $\lambda = 5460$ Å.

Hertel's observation^{33a} that addition of inert gases increases the quantum yield may be explained as caused by either an induced predissociation, which increases the number of chains started, or by retardation of the diffusion of the atoms to the walls. The latter effect would increase the observed rate by decreasing the rate of the chain terminating step. Parallel experiments in both regions of the spectrum would decide which explanation is correct.

11.35 Formation of HCl in mixtures of ICl, H₂, and Cl₂.

Rollefson and Lindquist³⁸ found that, if a mixture of ICl, H₂, and Cl₂ is illuminated with light absorbed by the chlorine, HCl is formed. If only ICl absorbs the light, no detectable reaction occurs. The quantum yield of HCl formation is reduced to a very low value by the presence of ICl, probably on account of the removal of chlorine atoms by the reaction of $\text{ICl} + \text{Cl} \rightarrow \text{I} + \text{Cl}_2$. The fact that the chlorine atoms

³⁵ Semenoff, *Chemical Kinetics and Chain Reactions*, Oxford University Press, 1935, p. 112.

³⁶ F. W. Jones and Spooner, *Trans. Faraday Soc.*, **31**, 811 (1935).

³⁷ Aickin and Bayliss, *ibid.*, **33**, 1333 (1937).

³⁸ Rollefson and Lindquist, *J. Am. Chem. Soc.*, **52**, 2793 (1930); **53**, 1184 (1931).

formed by the photodissociation of ICl did not react to give HCl was interpreted as due to a greater ease of removal of the atom formed in this case. Rollefson and Potts³⁹ discussed the possible interactions of normal and excited chlorine atoms with ICl molecules. They concluded that the excited atoms react less readily with ICl than the normal ones. The experimental results are explained on the basis that chlorine dissociates into one normal and one excited atom, whereas ICl dissociates into normal atoms; it is only the excited atom which survives long enough to react with hydrogen.

Mellor and Iredale,⁴⁰ and Ashley and West⁴¹ reported formation of I₂ and HCl on illumination of mixtures of ICl and hydrogen. The latter stated that, the purer the ICl used, the less the observed reaction. Franck and Rabinowitch⁴² found no reaction between ICl and hydrogen on excitation with an electric discharge.

11.4 Photochemical formation of phosgene. The reaction of carbon monoxide and chlorine to form COCl₂ is another example of a chain reaction which has been studied repeatedly. The first kinetic studies on this reaction were carried out with constant light intensity and approximately equal pressures of the two gases. They showed the overall rate to be of second order.⁴³ Chapman and Gee^{43b} reported a marked retardation by various impurities, especially oxygen. The chain character of the reaction was established by Bonhoeffer⁴⁴ and by Bodenstein,⁴⁵ who reported quantum yields of 2700 and 1000–1500, respectively. The latter also showed that a chain reaction occurs in the presence of relatively large oxygen concentrations; however, under these conditions the principal product is not phosgene but carbon dioxide. The two reactions are closely correlated, although

³⁹ Rollefson and Potts, *J. Chem. Phys.*, **1**, 400 (1933).

⁴⁰ Mellor and Iredale, *Nature*, **127**, 93 (1931).

⁴¹ Ashley and W. West, *ibid.*, **127**, 308 (1931).

⁴² Franck and Rabinowitch, *Z. Elektrochem.*, **36**, 794 (1930).

⁴³ (a) Wildermann, *Z. physik. Chem.*, **42**, 257 (1903); (b) Chapman and Gee, *J. Chem. Soc.*, **99**, 1726 (1911).

⁴⁴ Bonhoeffer, *Z. Physik*, **13**, 94 (1923).

⁴⁵ Bodenstein, *Rec. trav. chim.*, **41**, 585 (1922).

no complete mechanism has been devised for the carbon dioxide formation.

In the first of a series of papers on this subject, Bodenstein ⁴⁶ showed that the second order law previously reported is an approximation of a more complex rate law. By varying the concentrations of carbon monoxide and chlorine over a wide range, the correct law was found to be

$$\frac{d(\text{COCl}_2)}{dt} = kI_{\text{abs}}^{1/2}(\text{CO})^{1/2}(\text{Cl}_2) \quad 11-19$$

The rate decreases about 15 per cent when the temperature is raised from 10° to 40°C. Bodenstein and Onoda ⁴⁷ reported that, at temperatures around 300°C., the rate law changes to

$$\frac{d(\text{COCl}_2)}{dt} = kI_{\text{abs}}(\text{CO})(\text{Cl}_2) \quad 11-20$$

although the data could be fitted almost as well with some slightly different equations. The high temperature reaction is not affected by oxygen, nor does any sensitized carbon dioxide formation occur. Later Schumacher and Stieger ⁴⁸ found that, at low pressures, the rate law at ordinary temperature changes to the high temperature form.

The sensitized carbon dioxide formation was studied more extensively by Schumacher, ⁴⁹ who reported a dependence of the rate on $(\text{CO})^{1/2}$ and $(\text{Cl}_2)^{0.71}$ at constant light intensity. Such a law could not hold over a wide range of conditions. Further investigation by Schumacher and Stieger ⁵⁰ demonstrated two limiting laws at constant light intensity:

$$\frac{d(\text{CO}_2)}{dt} = k(\text{CO})^{1/2}(\text{Cl}_2)^{1/2} \quad (\text{at high pressures}) \quad 11-21$$

$$\frac{d(\text{CO}_2)}{dt} = k(\text{CO})^{1/2}(\text{Cl}_2) \quad (\text{at low pressures}) \quad 11-22$$

⁴⁶ Bodenstein, *Z. physik. Chem.*, **130**, 422 (1927).

⁴⁷ Bodenstein and Onoda, *ibid.*, **131**, 153 (1927).

⁴⁸ Schumacher and Stieger, *ibid.*, **B13**, 157 (1931).

⁴⁹ Schumacher, *ibid.*, **129**, 241 (1927).

⁵⁰ Schumacher and Stieger, *ibid.*, **B13**, 169 (1931).

Both of these laws were obtained in the presence of a large excess of oxygen. The quantum yield is 1000 at $(\text{Cl}_2) = (\text{O}_2) = (\text{CO}) = \frac{1}{2}$ atmosphere. The rate decreases 5 per cent for a 10-degree rise in temperature.

Rollefson⁵¹ studied the relative rates of formation of carbon dioxide and phosgene in mixtures of carbon monoxide, chlorine, and oxygen. He found that the relative amounts of oxygen and chlorine reacting are given by the equation

$$\frac{d(\text{O}_2)}{d(\text{O}_2) + d(\text{Cl}_2)} = \frac{1}{1 + k \frac{(\text{Cl}_2)}{(\text{O}_2)}} \quad 11-23$$

in which $k = 0.2$ at 20°C . and over a temperature range is given by $k = 30e^{-3000/RT}$. According to this equation, the numbers of moles of oxygen and chlorine which react at 20°C . are equal if the chlorine pressure is five times the oxygen pressure. At high relative oxygen pressures, the formation of carbon dioxide increases and in the limit no phosgene is formed.

Several mechanisms may be written which will account for these observations. In order to restrict the possibilities further, Rollefson and Montgomery⁵² studied the oxidation of phosgene to carbon dioxide and chlorine in reaction mixtures containing both chlorine and oxygen. The rate of the reaction was shown to be given by

$$-\frac{d(\text{COCl}_2)}{dt} = kI_{\text{abs}} \frac{1}{1 + k' \frac{(\text{Cl}_2)}{(\text{O}_2)}} \quad 11-24$$

in which k' was found to be identical with k in equation 11-23 at all temperatures. Furthermore, Rollefson and Montgomery⁵³ showed that, if phosgene is introduced into a vessel containing carbon monoxide and oxygen and the mixture is illuminated with light absorbed by the phosgene, a sensitized formation of carbon dioxide occurs. The quantum yield for this reaction is approximately the same

⁵¹ Rollefson, *J. Am. Chem. Soc.*, **55**, 148 (1933).

⁵² Rollefson and Montgomery, *ibid.*, **55**, 142 (1933).

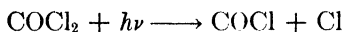
⁵³ Rollefson and Montgomery, *ibid.*, **55**, 4036 (1933).

as for the chlorine-sensitized reaction, and the rate law at high oxygen pressures is

$$\frac{d(\text{CO}_2)}{dt} = kI_{abs}^{1/2}(\text{CO})^{1/2} \quad 11-25$$

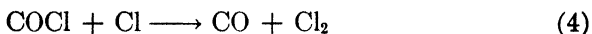
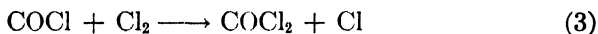
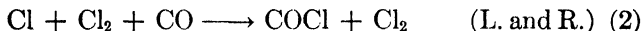
This equation is identical in form with that found by Schumacher and Stieger for the chlorine-sensitized reaction.

The close correspondence between the results obtained in these systems in which phosgene is the absorbing substance and those in which chlorine is the absorber indicates that the same intermediate is obtained both from phosgene and from carbon monoxide and chlorine. The predissociation limit in phosgene at $\sim 2700 \text{ \AA}$ is interpreted as corresponding to the reaction



This process is analogous to the dissociation of formaldehyde into H and HCO at approximately the same wave length (cf. § 8.72). It seems reasonable to assume that the intermediate which must be considered in order to explain the facts that have been presented in the preceding paragraphs, is the molecule COCl. The discussion of possible mechanisms will be limited to those which include this molecule.

Two mechanisms have been presented that fulfill this condition.⁵⁴ Both assume dissociation of chlorine as the first step, and a reaction between COCl and Cl as the chain terminating step. The steps are represented by the following equations:



The observed rate law at moderate pressures may be obtained from this set of reactions using either (2) or (2a).

⁵⁴ (a) Bodenstein, Lenher, and Wagner, *Z. physik. Chem.*, **B3**, 459 (1929);
(b) Lenher and Rollefson, *J. Am. Chem. Soc.*, **52**, 500 (1930).

These two equations show the difference between the assumed mechanisms. If (2a) is used, it must be assumed that equilibrium is maintained between Cl and CO and COCl. For this condition to hold, reaction (3) must be slow as compared to the reverse of (2a).⁵⁵

If reaction (2) is used instead of (2a), it is unnecessary to assume such an equilibrium, but it is necessary to assume that Cl₂ has a specific action as the third body in the formation of COCl. The possibility of such a specific action is supported by Rollefson and Eyring's calculations²⁰ on the stability of the Cl₃ molecule. Craggs and Allmand found it necessary to assume such a molecule in order to account for their results on the hydrogen-chlorine reaction. It has been assumed for a number of other reactions, although in some cases alternative explanations have been available. In this case it is to be noted that the mechanism does not require the formation of Cl₃ as a stable molecule but merely that there shall be enough of a tendency in that direction to cause Cl₂ to have the specific action indicated. Of course, if Cl₃ is formed as a stable molecule, reaction (2) should be replaced by the equilibrium $\text{Cl} + \text{Cl}_2 \rightleftharpoons \text{Cl}_3$, followed by the reaction of Cl₃ with CO. The rate equations deduced⁵⁶ from the mechanisms are:

$$\frac{d(\text{COCl}_2)}{dt} = \sqrt{\frac{k_2 k_3}{k_4}} I_{abs}^{1/2} (\text{CO})^{1/2} (\text{Cl}_2) \quad (\text{L. and R.}) \quad 11-26$$

$$\frac{d(\text{COCl}_2)}{dt} = \frac{k_3}{K_{2a}^{1/2} k_4^{1/2}} I_{abs}^{1/2} (\text{CO})^{1/2} (\text{Cl}_2) \quad (\text{B. et al.}) \quad 11-27$$

⁵⁵ The mechanism as originally given by Bodenstein, Lenher, and Wagner did not use reaction (3) but wrote, instead, $\text{CO} + \text{Cl} + \text{Cl}_2 \rightarrow \text{COCl}_2 + \text{Cl}$. More recent papers from that laboratory have written the mechanism as indicated. Cf. Bodenstein, *Naturwissenschaften*, **23**, 10 (1935).

⁵⁶ The equations may be deduced in a manner analogous to that which has been employed in discussing the hydrogen-chlorine and hydrogen-bromine reactions, or by setting up the rate equations for the individual steps and setting

$\frac{d(\text{Cl})}{dt} = -\frac{d(\text{Cl})}{dt}$ and $\frac{d(\text{COCl})}{dt} = -\frac{d(\text{COCl})}{dt}$; i.e., it is assumed that the

rates of formation and removal of the intermediates are fast as compared to the net rates of change of the concentrations of these intermediates. In this way, if we have n intermediates, we obtain n equations and can solve for the concentrations in terms of measured quantities.

In equation 11-27, K_{2a} is the equilibrium constant for reaction (2a); the other k factors have the usual significance. In both derivations it is assumed that a term due to (4) can be neglected when it appears in a sum with one due to (3). This is obviously justified, since the quantum yield shows that (3) occurs about 1000 times as often as (4). The change in the form of the rate law at low pressures or high temperatures can be accounted for by replacing the chain terminating step (4) by a wall reaction.

The steps necessary to account for the formation of carbon dioxide when oxygen is introduced into the reaction mixture have never been successfully worked out. Both mechanisms assume that the oxygen enters the reaction chain by attacking the COCl



While the products are not necessarily those indicated in reaction (5), ultimately CO_2 is formed and a chlorine atom is regenerated or the chain is terminated. The failure of oxygen to affect the reaction at high temperatures is attributed by Rollefson to the fact that the reaction of COCl with Cl_2 is faster than that with O_2 at those temperatures. Bodenstein assumes that the equilibrium (2a) is shifted toward CO and Cl to such an extent that COCl does not need to be considered. He assumes that, under these conditions, phosgene is formed in some way, such as $\text{CO} + \text{Cl} + \text{Cl}_2 \rightarrow \text{COCl}_2 + \text{Cl}$. Rollefson's equation for the relative amounts of CO_2 and COCl_2 formed follows directly from a consideration that reactions (3) and (5) suffice to determine the ultimate fate of the CO molecules which react. The rather small difference between the rates of reactions (3) and (5) raises a serious question as to the validity of the equilibrium assumed in (2a). On the basis of that assumption, the only way oxygen can reduce the rate of formation of phosgene is to reduce the concentration of COCl to a corresponding fraction of its equilibrium concentration. The observed decrease in the rate of formation of phosgene is very much greater than is compatible with the observed relative rates of reactions (3) and (5).

This difficulty has been ignored by Bodenstein⁵⁰ and his students, who have advanced as the principal argument for their mechanism a set of values for the rate constants of the individual steps (3) and (4) and the equilibrium constant K_{2a} . The details of these calculations have never been published; however, it is obvious that, since both theoretical rate equations contain three constants, any set of data which permits the calculation of the constants for one mechanism also permits the calculation for the other. Of course, if assumptions are involved in the calculation, they may have to be different for the two mechanisms. The most recent papers dealing with this reaction have not altered the status of the problem. It is doubtful whether a completely satisfactory mechanism can be written until the steps in the associated chlorine-sensitized and phosgene-sensitized formation of carbon dioxide are known.⁵⁷

11.5 Chlorination of methane and its derivatives. Coehn and Cordes⁵⁸ made a semiquantitative study of the chlorination of methane, methyl chloride, methylene chloride, and chloroform. Carbon tetrachloride and hydrogen chloride are the ultimate products, but the reactions proceed in stages. If methane is the initial carbon compound, all of the possible chlorination products are formed almost simultaneously in the reacting mixture and it is only with excess chlorine that carbon tetrachloride becomes the sole chlorinated product. The quantum yields of all of the possible reactions are of the order of 10^3 or 10^4 . As might be expected with reaction chains of this length, the reactions are quite susceptible to inhibition by impurities. The number of parallel reactions occurring in these mixtures renders it impossible to present any simple interpretation of the results.

Schwab and Heyde⁵⁹ studied the rate of the photochemical

⁵⁷ Rollefson, *Z. physik. Chem.*, **B37**, 472 (1937); Bodenstein, Brenschede, and Schumacher, *ibid.*, **28**, 81 (1935); Bodenstein, Schumacher, and Brenschede, *ibid.*, **35**, 382 (1937); Rollefson, *J. Am. Chem. Soc.*, **56**, 579 (1934). Numerical values for the constants have appeared in a recent paper by Bodenstein, Schumacher, and Brenschede, *Z. physik. Chem.*, **B40**, 121 (1938).

⁵⁸ Coehn and Cordes, *Z. physik. Chem.*, **B9**, 1 (1930).

⁵⁹ Schwab and Heyde, *Z. physik. Chem.*, **B8**, 147 (1930).

reaction of chlorine with chloroform. Their rates were represented by the equation

$$\frac{d(\text{CCl}_4)}{dt} = \frac{kI_{\text{abs}}(\text{Cl}_2)(\text{CHCl}_3)}{(\text{Cl}_2) + k'(\text{HCl})}[1 + k''(\text{Cl}_2)] \quad 11-28$$

Schumacher and Wolff ⁶⁰ reported a much simpler rate law

$$\frac{d(\text{CCl}_4)}{dt} = k(\text{Cl}_2)^{1/2}I_{\text{abs}}^{1/2} \quad 11-29$$

The two equations differ so greatly that additional experiments are necessary. The second equation would normally be preferred, since it involves only one constant. On the other hand, it is obvious that the rate must depend on the chloroform concentration under some conditions.

The addition of oxygen to any of these reaction mixtures retards the chlorination reaction and introduces a sensitized oxidation. Jones and Bates ⁶¹ found the rate of formation of methyl chloride from methane and chlorine at constant light intensity in the presence of some oxygen to be

$$\frac{d(\text{CH}_3\text{Cl})}{dt} = \frac{k(\text{CH}_4)(\text{Cl}_2)^2}{(\text{O}_2)[k'(\text{CH}_4) + (\text{Cl}_2)]} \quad 11-30$$

This equation bears a close resemblance to those which have been proposed for the action of oxygen on the hydrogen-chlorine reaction. Since the products were not identified, it is not possible to specify the mechanism of the inhibition. Probably the oxygen reacts with methyl radicals formed by the reaction of a chlorine atom with a methane molecule. Schumacher and Wolff ⁶² showed that the addition of considerable pressures of oxygen to illuminated mixtures of chloroform and chlorine caused the oxidation of the chloroform to phosgene. They expressed the belief that the oxygen reacts with CCl_3 radicals, but were unable to set up a mechanism which would account for their data.

11.51 Reaction between formaldehyde and chlorine. Krauskopf and Rollefson ⁶³ found that formaldehyde and

⁶⁰ Schumacher and Wolff, *Z. physik. Chem.*, **B25**, 161 (1934).

⁶¹ L. T. Jones and Bates, *J. Am. Chem. Soc.*, **56**, 2282 (1934).

⁶² Schumacher and Wolff, *Z. physik. Chem.*, **B26**, 453 (1934).

⁶³ Krauskopf and Rollefson, *J. Am. Chem. Soc.*, **56**, 2542 (1934).

chlorine react to give carbon monoxide and hydrogen chloride as the ultimate products. Although no direct measurements of the quantum yield were made, the high rate of reaction and the fact that the formation of phosgene from the carbon monoxide and excess chlorine was relatively slow indicate that the quantum yield is very high. It was demonstrated that the reaction proceeds in two stages. The first stage causes no net pressure change but must evolve considerable heat, as indicated by a large Draper effect. The product formed in this stage was isolated and identified as formyl chloride. The second stage is the decomposition of the formyl chloride into carbon monoxide and hydrogen chloride. This reaction proceeds in the dark on the walls of the reaction vessel, and the rate is dependent on the condition of the walls. In the presence of excess chlorine, the reaction proceeds much more rapidly via a sensitized process. The concentration of formyl chloride present in the course of an experiment varies from a low value in the presence of excess chlorine to a high one if excess formaldehyde is used.

11.52 Formic acid and chlorine. H. L. West and Rollefson⁶⁴ showed that, on illumination with visible light, chlorine reacts with formic acid to form carbon dioxide and hydrogen chloride. Some evidence was obtained for the formation of chloroformic acid as an intermediate, but no large amounts of this substance were obtained. The reaction mixtures contained both single and double molecules of formic acid, both of which react readily with the chlorine. The rate is expressed approximately by

$$-\frac{d(\text{Cl}_2)}{dt} = kI_{abs}^{1/2} [(\text{HCOOH}) + ((\text{HCOOH})_2)] \quad 11-31$$

The exponent of I_{abs} changed from one-half to one as the chlorine pressure or light intensity was lowered. The quantum yields obtained were about 2000.

11.53 Bromotrichloromethane and chlorine. This reaction was first studied in CCl_4 solution by Noddack,⁶⁵

⁶⁴ H. L. West and Rollefson, *ibid.*, **58**, 2140 (1936).

⁶⁵ Noddack, *Z. Elektrochem.*, **27**, 359 (1921).

who reported a quantum yield ranging from 0.2 to 1.0. In a later study Grüss⁶⁶ obtained quantum yields of 0.88 ± 0.25 , independent of the concentration. In both of these investigations it was assumed that the reaction products were carbon tetrachloride and bromine, and the reaction was followed by measuring the increase in the absorption of light by the reacting mixture. Recently it has been shown⁶⁷ that, under the conditions prevailing in these experiments, bromine is converted almost completely into bromine chloride. The latter compound has a much lower absorption coefficient than bromine at the wave lengths which were used by Noddack and by Grüss in their analyses. Consequently the amount of reaction which occurred in their experiments was actually considerably greater than they believed. Vesper and Rollefson⁶⁸ recalculated their data and showed that the quantum yield is of the order of 10. The latter also studied the gas phase reaction and found quantum yields ranging from 10 to 30, depending on the pressures of the reactants and bromine chloride. Their results indicate that the reaction is much more complex than was previously thought.

11.6 Alkyl radicals and hydrogen atoms as chain carriers.

Leermakers⁶⁹ showed that, at temperatures above 80°C., the photochemical decomposition of acetaldehyde is a chain reaction. Values of the quantum yield as high as 300 were obtained at 309.5°C. The rate of the chain reaction for $\lambda = 3130 \text{ Å}$ is given by

$$\frac{d(\text{CO})}{dt} = 1 \times 10^6 e^{-10000/RT} \sqrt{I_{abs}} (\text{CH}_3\text{CHO}) \quad 11-32$$

At low temperatures, correction must be made for the small amount of reaction which does not occur through the chain mechanism. The essential features of the mechanism are: (1) formation of radicals by the photodissociation of the

⁶⁶ Grüss, *ibid.*, **29**, 144 (1923).

⁶⁷ Blair and Yost, *J. Am. Chem. Soc.*, **55**, 4489 (1933); Vesper and Rollefson, *ibid.*, **56**, 620 (1934).

⁶⁸ Vesper and Rollefson, *ibid.*, **56**, 1455 (1934).

⁶⁹ Leermakers, *J. Am. Chem. Soc.*, **56**, 1537 (1934).

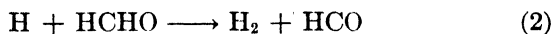
aldehyde molecule; (2) catalysis of the decomposition of other aldehyde molecules by these radicals; (3) their removal by a combination of two radicals. These assumptions suffice to determine the experimental rate law.

Leermakers⁷⁰ has also studied the decomposition of dimethyl ether photosensitized by acetone. In this case it is assumed that the absorption of light by the acetone produces free radicals, which in turn catalyze the decomposition of the ether. The radicals do not catalyze the decomposition of acetone below 400°C. In these experiments the temperatures ranged from 270°C. to 403°C. The rate of decomposition of the ether, as measured by the methane formed, is expressed by

$$\frac{d(\text{CH}_4)}{dt} = 10^4 e^{-16000/RT} \sqrt{\frac{I_{abs}}{(\text{acetone})}} (\text{ether}) \quad 11-33$$

Leermakers set up a mechanism from which he calculated the constant in the above equation from activation energies available in the literature. The calculated value was $10^7 e^{-20000/RT}$. In view of the numerous assumptions made in the calculation, Leermakers considered the agreement satisfactory. The experimental observations do not suffice to determine the steps in the mechanism uniquely.

Akeroyd and Norrish⁷¹ have also studied the high temperature photolysis of formaldehyde, acetaldehyde, and acetone. The first two were found to be chain reactions, but the last was not. They give the heats of activation for the reactions



as 9.8 and 16.2 kcal. respectively.

Carruthers and Norrish⁷² found that illumination of mixtures of formaldehyde and oxygen set up a chain reaction. The products formed were carbon dioxide, carbon monoxide, water, and hydrogen. These could be accounted for by

⁷⁰ Leermakers, *J. Am. Chem. Soc.*, **56**, 1899 (1934).

⁷¹ Akeroyd and Norrish, *J. Chem. Soc.*, 890 (1936).

⁷² Carruthers and Norrish, *J. Chem. Soc.*, 1036 (1936).

assuming that the formaldehyde is first oxidized to formic acid and that this compound is then photochemically decomposed (cf. § 8.8). The quantum yield varies somewhat with the composition of the reaction mixture; for equal pressures of the reactants, $\gamma = 12.6$ and for $(\text{HCHO})/(\text{O}_2) = 2$, $\gamma = 9.0$. No evidence was found for the production of a peroxide or peroxyacid.

CHAPTER XII

ADDITION REACTIONS AND ASSOCIATED PHENOMENA

12.1 Introduction. The addition of two molecules to form a single molecule is often accelerated by illumination of the reaction mixture with light absorbed by one or both of the reactants. The activating influence of the light may depend upon the formation of an atom or radical which "catalyzes" the addition, or it may depend upon an activation of one of the molecules which enables it to add the other readily.

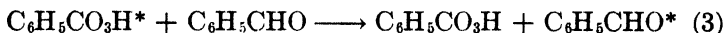
It has already been pointed out (§4.1) that a photo-activated molecule must react with practically no heat of activation if a high yield of products is to be obtained. In a number of reactions for which such a primary step has been assumed, a secondary chain process results in a high quantum yield. In these cases it cannot be said with certainty that the action of light is merely an activation of the absorbing molecule; however, the mechanism must be considered plausible until definite proof to the contrary is obtained. Many oxidations are of this type. The other type (namely, that in which an atom or radical produced by the photodissociation of an absorbing molecule is the "catalyst" for the addition reaction) is especially common in reactions involving the halogens. The detailed mechanisms of a number of such reactions are discussed in this chapter. Unfortunately, in many cases the data are insufficient for a unique specification of the mechanism. In those cases any mechanism set up must be considered as essentially schematic.

12.2 Photo-oxidation of acetaldehyde. The initial state in this reaction appears to be the formation of peroxyacetic acid. A secondary reaction leads to the formation of di-

acetyl peroxide as the principal product.¹ The quantum yield of the reaction was estimated as 10^3 by Bowen and Tietz, but a more direct determination by Carruthers and Norrish indicated a much lower value, ~ 20 in terms of diacetyl peroxide produced.

No mechanism has been presented for the photochemical reaction, although one has been set up for the thermal reaction which also proceeds through peroxyacetic acid.² In that case it is assumed that an activated aldehyde molecule adds a molecule of oxygen to form an activated peroxyacetic acid molecule, which sets up a series of reactions. In the photochemical reaction there is considerable doubt as to how many photoactivated molecules survive long enough to react with oxygen. Some of them certainly decompose to give free radicals (cf. § 8.72), which may react with the oxygen. On the other hand, the parallelism between fluorescence and polymerization of acetaldehyde indicates that some of the photoactivated molecules survive long enough to react with other molecules.^{2a} Further work is required before any conclusions can be drawn with regard to the steps in the reaction chain.

12.21 Photo-oxidation of benzaldehyde. Bäckström³ has studied both the thermal and the photochemical oxidations of benzaldehyde in solution. The chain length is the same for both methods of excitation, $\gamma = 10^4$. Peroxybenzoic acid is the principal product. The primary activation process is supposed to be the same for the thermal and the photochemical reactions. For the photochemical mechanism, Bäckström and Beatty⁴ suggest:



¹ (a) Bowen and Tietz, *J. Chem. Soc.*, 234 (1930); (b) Carruthers and Norrish, *ibid.*, 1036 (1936).

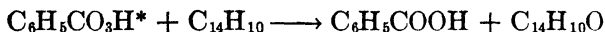
² Bodenstein, *Sitzb. preuss. Akad. Wiss.*, 73 (1931).

^{2a} Rollefson, *J. Phys. Chem.*, **41**, 259 (1937).

³ Bäckström, *J. Am. Chem. Soc.*, **52**, 974 (1930).

⁴ Bäckström and Beatty, *J. Phys. Chem.*, **35**, 2530 (1931).

The reaction chain is broken by some inhibitor molecule. With anthracene as the inhibitor, Bäckström and Beatty give the following reaction:



In support of the assumption of an activated form of the peroxyacid, reference is made to the observation of Jorissen and van der Beck⁵ that a solution in which benzaldehyde is being oxidized is a better oxidizing agent than the peroxyacid formed in the reaction. Bäckström and Beatty also concluded that reaction (3) in the mechanism proceeds only once in 1000 collisions.

In a formal sense, the steps listed above represent the course of the reaction. The nature of the initial step must be considered somewhat uncertain in the light of the work which has appeared on the photodecomposition of the aldehydes (cf. § 8.72). If it can be demonstrated that the initial stage is a dissociation, the whole mechanism will have to be revised.

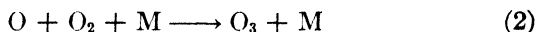
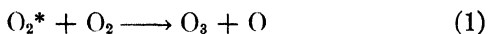
12.3 Photochemical formation of ozone. Ozone is both formed and decomposed by ultraviolet light. This fact has complicated the experimental conditions so that most of the recent work has been concerned primarily with the decomposition process (cf. § 7.2). The formation from oxygen occurs over a wide region of the spectrum at $\lambda < 2530 \text{ \AA}$.⁶ Warburg's observations^{6a} extended over pressures up to 300 atmospheres and definitely established the formation of ozone at $\lambda \sim 2530 \text{ \AA}$. Since the dissociation energy of oxygen into normal atoms corresponds to $\lambda = 2420 \text{ \AA}$, there has been some speculation as to the nature of the primary step at this wave length. Some evidence has been presented which indicates that the absorption in this region is at least partially due to an O_4 molecule.⁷ The bands in this

⁵ Jorissen and van der Beck, *Rec. trav. chim.*, **49**, 138 (1930).

⁶ (a) Warburg, *Z. Elektrochem.*, **27**, 133 (1921); (b) Weigert, *Z. physik. Chem.*, **80**, 78 (1912); (c) Regener, *Ann. Physik*, **20**, 1033 (1906).

⁷ Wulf, *Proc. Nat. Acad.*, **14**, 356, 603 (1928). Cf. also Bonhoeffer and Harteck, *Grundlagen der Photochemie*, Theodor Steinkopf, Dresden, 1933, p. 110.

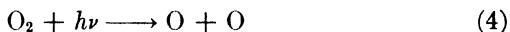
region are attributed by Herzberg⁸ to a ${}^3\Sigma_g^- \rightarrow {}^3\Sigma_u^+$ transition of the O_2 molecule. The small absorption is associated with the nature of this transition, which is contrary to the selection rules. If it is assumed that the absorption of $\lambda = 2530 \text{ \AA}$ transfers the O_2 to the ${}^3\Sigma_u^+$ state, then the formation of ozone may be written



On the other hand, if O_4 is the absorbing molecule, the initial stage may be



Still another possibility, which appears to have been overlooked, is that the effective absorption may be due to O_2 molecules in vibrational states $v'' \geq 1$, which would permit the direct dissociation of the molecules.



Either reaction (1) or (3) followed by (2) would give a maximum quantum yield of 2. Reaction (4) followed by (2) gives a value of 3. The yield actually found by Warburg^{6a} at $\lambda = 2530 \text{ \AA}$ was 1.65 at a pressure of 125 kg./cm.², and 0.87 at 300 kg./cm.² The available data do not permit the exact determination of the mechanism.

At shorter wave lengths than 2420 $\text{\AA}$, the dissociation of O_2 is always possible as the primary step. It is not known whether, in the region between 2420 $\text{\AA}$ and 1751 $\text{\AA}$, the effective absorption is that due to the continuum which is present or the bands, or both. The observed facts are satisfactorily accounted for by assuming as the initial step reaction (4) followed by (2). Warburg's values for the quantum yield at $\lambda = 2070 \text{ \AA}$ are 3.0 at 125 kg./cm.², and 2.3 at 300 kg./cm.² Vaughan and Noyes⁹ found 3.0 at $\lambda = 1700$ to 1900 $\text{\AA}$.

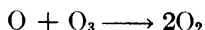
Eucken and Patat¹⁰ have studied the temperature

⁸ Herzberg, *Naturwissenschaften*, **20**, 577 (1932).

⁹ Vaughan and Noyes, *J. Am. Chem. Soc.*, **52**, 559 (1930).

¹⁰ Eucken and Patat, *Z. physik. Chem.*, **B33**, 459 (1936).

dependence of the formation of ozone at $\lambda = 1720 \text{ \AA}$. They found a temperature coefficient for the back reaction



corresponding to an activation energy of 6.2 kcal.

12.4 Addition reactions involving the halogens. Many investigations have been made of the addition of the halogens to molecules containing double or triple bonds. The reactions are often complicated by the simultaneous occurrence of a substitution reaction or by the presence of an appreciable thermal reaction. Furthermore, the relatively high boiling points of the products have in many cases necessitated the limitation of the experiments to solutions or to gases at temperatures appreciably higher than room temperature. The quantum yields are usually high and the reactions are correspondingly sensitive to small quantities of inhibitors. Oxygen usually enters into a halogen-sensitized oxidation reaction, which becomes practically the only reaction occurring at high oxygen concentrations. Mechanisms have been set up for many of the systems, but usually the data are insufficient to distinguish between a given mechanism and others which may be proposed. There can be little doubt that the action of the light absorbed is to produce halogen atoms which enter into secondary chain reactions. The chains are broken in a variety of ways, such as by impurities, by combination of two atoms or two other intermediates, or at the walls of the reaction vessel.

12.41 Chlorination of ethylene. Chlorine adds to ethylene to form ethylene chloride at a measurable rate in the dark but the reaction is extremely slow at low pressures. Stewart and Weidenbaum¹¹ measured the photochemical rate with each gas at a pressure of $\sim 13 \text{ mm. Hg}$. The rate is proportional to the rate of absorption of light. Such a law can be obtained from a great variety of mechanisms. The only requirement imposed by the rate law is that the chain terminating step shall be of the first order with respect to chlorine atoms or some other intermediate.

¹¹ T. D. Stewart and Weidenbaum, *J. Am. Chem. Soc.*, **57**, 2036 (1935).

Stewart and Weidenbaum also made the observation that, if mixtures of hydrogen, ethylene, and excess chlorine are illuminated with light absorbed by the chlorine, the ethylene is completely converted into ethylene chloride, without appreciable formation of hydrogen chloride. This fact must be interpreted as showing that chlorine atoms react much faster with ethylene than with hydrogen. Since both reactions are bimolecular and the heat of activation of the latter is known to be 6 kcal. (cf. § 11.3), it may be concluded that the reaction of the atoms with ethylene requires little, if any, activation energy. Under such conditions the concentration of the atoms would be too low for the rate of recombination to be appreciable; hence it is not surprising to find that the experimental rate law corresponds to the removal of the atoms in a first order reaction.

12.42 Addition of chlorine and bromine to tetrachloroethylene. The only possible reaction between pure tetrachloroethylene and chlorine is the formation of hexachloroethane. This reaction has been studied both in the gas phase and in solution in carbon tetrachloride. Leermakers and Dickinson¹² found that the quantum yield for the reaction in solution ranges from 300 to 2500. The rate of the reaction is given by

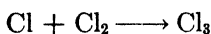
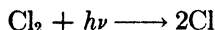
$$-\frac{d(\text{Cl})_2}{dt} = 5.1 I_{\text{abs}}^{1/2} (\text{Cl}_2) \left[1 + 0.4 \frac{(\text{Cl}_2)}{(\text{C}_2\text{Cl}_4)} \right]^{-1/2} \quad 12-1$$

Dickinson and Carrico¹³ found that, in the gas phase, the quantum yield is slightly less than in solution and that the rate is given by the more simple expression

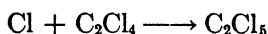
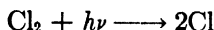
$$-\frac{d(\text{Cl}_2)}{dt} = k I_{\text{abs}}^{1/2} (\text{Cl}_2) \quad 12-2$$

This rate equation may be deduced from either of the following mechanisms:

MECHANISM A

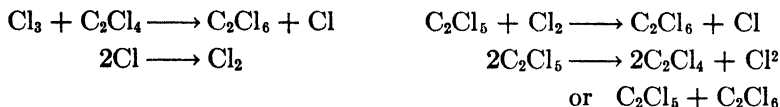


MECHANISM B

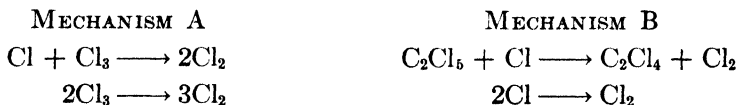


¹² Leermakers and Dickinson, *J. Am. Chem. Soc.*, **54**, 4648 (1932).

¹³ Dickinson and Carrico, *ibid.*, **56**, 1473 (1934).



In order to account for the indicated action of C_2Cl_4 in the reaction in solution, the additional steps



were considered.

The reaction is strongly inhibited by oxygen, both in the gas phase¹³ and in solution.¹⁴ At high concentrations of oxygen the chlorination reaction becomes negligible with respect to an oxidation reaction in which trichloroacetyl chloride is the principal product and some phosgene is also formed. The quantum yield of this reaction in the gas phase is ~ 300 molecules of C_2Cl_4 oxidized for each quantum absorbed. In solution the yield is about 2. The gas phase reaction shows no marked dependence either on the concentrations or on the light intensity. Over a moderate range of conditions in solution, the rate is expressed by

$$-\frac{d(\text{C}_2\text{Cl}_4)}{dt} = kI_{abs} \left[1 + b(\text{C}_2\text{Cl}_4)^{1/2} \right] \quad 12-3$$

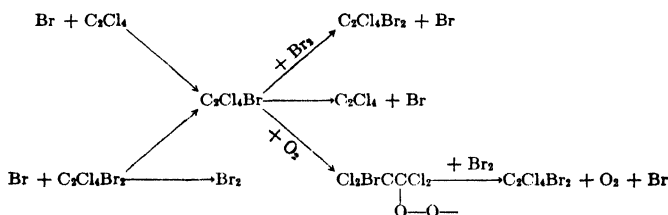
This equation fails at high C_2Cl_4 concentrations. No mechanism has been devised which will account for these observations. The nature of the products suggests that the oxygen enters the reaction in a step involving some intermediate, such as C_2Cl_5 .

The addition of bromine to C_2Cl_4 to form $\text{C}_2\text{Cl}_4\text{Br}_2$ has been studied in detail by Willard and Daniels.¹⁵ There is a slight but unimportant dark reaction in solution. Although the data were not summarized in the form of a rate law, it may be said that the rate is approximately proportional to the rate of absorption of light and almost independent of the concentration of C_2Cl_4 . Variation of the concentration

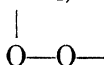
¹⁴ Dickinson and Leermakers, *J. Am. Chem. Soc.*, **54**, 3852 (1932).

¹⁵ Willard and Daniels, *J. Am. Chem. Soc.*, **57**, 2240 (1935).

of C_2Cl_4 in CCl_4 solution from 0.17 to 5.0 moles per liter increased the rate only 2.5 times. The quantum yields varied with individual fillings of the reaction cell and with the concentration of the products. The highest value observed was 24, and the lowest 0.009. Small amounts of oxygen accelerate the bromination reaction. With the addition of large amounts of oxygen, the rate of bromination approaches zero and a bromine-sensitized photo-oxidation occurs. The course of the bromination reaction after the formation of bromine atoms was represented schematically by Willard and Daniels as follows:



The accelerating effect of oxygen is attributed to the longer life of the radical $\text{C}_2\text{BrCCCl}_2\cdot$, as compared with the radical



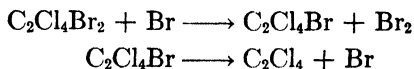
$\text{C}_2\text{Cl}_4\text{Br}\cdot$.

For the bromine-sensitized oxidation reaction, Willard and Daniels assumed an activated Br_2 molecule, which in turn activates an oxygen molecule (the oxygen reacting with the C_2Cl_4). However, it seems more probable that the oxygen reacts with some intermediate radical produced by Br atoms; such a mechanism is to be preferred since there is no other evidence that Br_2 molecules in an excited state are ever of importance in a photochemical reaction.

The retarding action of the product $\text{C}_2\text{Cl}_4\text{Br}_2$ was attributed by Willard and Daniels to a bromine-sensitized photo-decomposition of this molecule. The reaction has been studied more extensively by Carrico and Dickinson¹⁶ at temperatures up to 150°C . At the higher temperatures little or no addition of bromine to C_2Cl_4 occurs, but the

¹⁶ Carrico and Dickinson, *J. Am. Chem. Soc.*, **57**, 1343 (1935).

reverse reaction occurs as a bromine-sensitized process with a quantum yield ranging from 0.25 to 45. The reaction chains are assumed to consist of the repetition of the reactions



Although the data do not suffice for a quantitative check of the mechanism, the observed facts are at least qualitatively in accord with the ideas expressed.

12.43 Other reactions involving the addition of a halogen to an ethylenic linkage. Müller and Schumacher¹⁷ have studied the addition of chlorine to *cis* and *trans* dichloroethylene and to trichloroethylene. The rates of all three reactions are expressed by equations of the form

$$-\frac{d(\text{Cl}_2)}{dt} = kI_{abs}^{1/2}(\text{Cl}_2) \quad 12-4$$

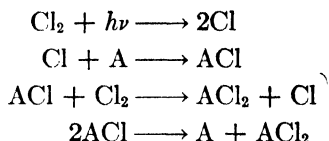
under their experimental conditions. The quantum yields of the reactions of the dichlorocompounds were the same; at $\lambda = 4360 \text{ \AA}$, chlorine pressure 100 mm., and a light absorption of $10^{16} \text{ } h\nu/\text{min.}$, the quantum yield is 7000 at 80°C . A small amount of substitution, ~ 1 per cent of the addition reaction, accompanied the main reaction. The temperature coefficient corresponds to an activation energy of 3.1 kcal. The quantum yield for the chlorination of trichloroethylene is 700 under the same conditions. The temperature coefficient is slightly higher than in the other cases, corresponding to an activation energy of 5.3 kcal.

Oxygen is a powerful inhibitor for all of these reactions and, if present at sufficient concentration, enters into a chlorine-sensitized photoreaction. Müller and Schumacher¹⁸ have studied the oxidation reaction in detail in the case of the trichloroethylene. The principal product is dichloroacetyl chloride. The rate is proportional to the light absorption, and the quantum yield is 40 at 95°C .

¹⁷ Müller and Schumacher, *Z. physik. Chem.*, **B33**, 285, 455 (1937).

¹⁸ Müller and Schumacher, *ibid.*, **B37**, 365 (1937).

No mechanism has been devised which fits the observations on the oxidations. The chlorination reactions are assumed to proceed according to the following general scheme:



Ghosh and Bhattacharyya¹⁹ have studied the addition of bromine to acetylene dichloride ($\text{C}_2\text{H}_2\text{Cl}_2$) both in the gas phase and in solution in carbon tetrachloride. The quantum yield is 2 to 4 in solution, and 100 to 260 in the gas phase. The following mechanism was written for the reaction:



These reactions lead to the rate equation

$$-\frac{d(\text{Br}_2)}{dt} = k_2 \left(\frac{I_{\text{abs}}}{k_4} \right)^{1/2} (\text{Br}_2) \frac{k_3(\text{A})}{k_3(\text{A}) + k_4} \quad 12-5$$

which the authors say is in agreement with their observations. Unfortunately, the experimental conditions were not varied sufficiently to test the factor $k_3(\text{A})/[k_3(\text{A}) + k_4]$. Without such a test it is impossible to distinguish between this rate equation and others deduced from other mechanisms. The reaction appears to be similar to the chlorine additions studied by Müller and Schumacher.

Very little is known about the addition of iodine to ethylene or similar compounds. DeRight and Wiig²⁰ illuminated solutions of ethylene and iodine in carbon tetrachloride at 25°C. with light of $\lambda \approx 7000 \text{ \AA}$. Ethylene iodide

¹⁹ Ghosh and Bhattacharyya, *Z. physik. Chem.*, **B32**, 145 (1936).

²⁰ DeRight and Wiig, *J. Am. Chem. Soc.*, **58**, 693 (1936).

was formed. The rate of the reaction is dependent on the ethylene and iodine concentrations. No experiments with other wave lengths which are absorbed by iodine have been carried out at this temperature.

Forbes and Nelson²¹ found that an addition reaction occurs when solutions of iodine and butene in methylene chloride or chloroform are illuminated at -60° to -90°C . The product decomposed on standing for one hundred hours at room temperature.

A preliminary communication by Ghosh and Bhattacharyya²² reports the photoaddition of iodine to dicyclopentadiene, β -amylene, and phenylacetylene in solution in carbon tetrachloride or benzene. The following statements are made concerning the reactions:

(1) The quantum yield is high, indicating a chain mechanism.

(2) The rates are proportional to the square root of the light absorbed and are almost independent of temperature.

(3) The rates are of the first order with respect to iodine.

(4) Photostationary states were found with β -amylene and dicyclopentadiene.

The addition of bromine to cinnamic acid has been studied repeatedly in carbon tetrachloride solutions. The reaction was believed to be purely photochemical, but recently Bauer and Daniels²³ have shown that, if oxygen is eliminated before mixing the reactants, the dark reaction is so fast that the color of bromine disappears within a few minutes. Apparently all the earlier work dealt with the oxygen-inhibited reaction. Any reproducibility of results in those experiments can probably be traced to the fact that the solutions were in equilibrium with the atmosphere and to a consequent approximate constancy of the oxygen concentration. The reaction is evidently much more complex than was previously believed.

The addition of chlorine to cinnamic acid was reported by

²¹ Forbes and Nelson, *ibid.*, **58**, 162 (1936).

²² Ghosh and Bhattacharyya, *Science and Culture*, **3**, 120 (1937).

²³ Bauer and Daniels, *J. Am. Chem. Soc.*, **56**, 2014 (1934).

Berthoud and Porret.²⁴ In view of the results just mentioned for the bromine addition, these experiments should be repeated with oxygen carefully excluded. It is improbable that chlorine would be any less reactive than bromine.

12.44 Addition of chlorine and bromine to acetylene.

Schlegel²⁵ reported that mixtures of pure acetylene and chlorine do not react in the dark but react at a measurable rate in diffuse daylight. Peters and Neumann²⁶ studied the photochemical reaction in an attempt to determine the most favorable conditions for the formation of dichloroethylene. Booher and Rollefson²⁷ attempted to study the kinetics of the reaction; however, preliminary experiments revealed a number of undesirable properties. First, an appreciable dark reaction occurs at temperatures high enough to prevent condensation of the products. Second, unless extreme care is taken as to the light intensity and relative concentrations of chlorine and acetylene, explosions occur with the formation of carbon and hydrogen chloride.

Bromine and acetylene react very slowly in the dark, even at 150°C. This reaction was studied from the kinetic standpoint by Booher and Rollefson.²⁷ The principal product is acetylene dibromide; with excess bromine, some acetylene tetrabromide is formed toward the end of the reaction. This secondary reaction is not complete but apparently proceeds to a photostationary state. The quantum yield for the formation of the acetylene dibromide is the same for $\lambda = 5791, 5461, \text{ and } 4358 \text{ \AA}$. At 150°C., $\gamma = 500$; at 21°C., $\gamma = 3200$. Both values were obtained with the bromine and acetylene pressures each $\sim 40 \text{ mm}$. The form of the rate law varies with the concentrations of the reactants; two limiting forms are given.²⁸ At high acetylene pressures,

$$-\frac{d(\text{Br}_2)}{dt} = \frac{k_1 I_{abs}}{1 + k' / (\text{Br}_2)} \quad 12-6$$

²⁴ Berthoud and Porret, *Helv. Chim. Acta*, **17**, 237 (1934).

²⁵ Schlegel, *Ann.*, **23**, 153 (1884).

²⁶ Peters and Neumann, *Z. angew. Chem.*, **45**, 261 (1932).

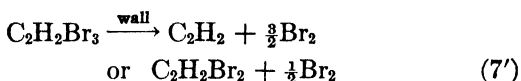
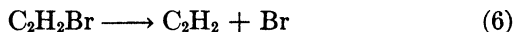
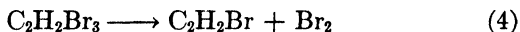
²⁷ Booher and Rollefson, *J. Am. Chem. Soc.*, **56**, 2288 (1934).

²⁸ These laws are not exactly those given by Booher and Rollefson but are equivalent to them.

and at low acetylene pressures,

$$-\frac{d(\text{Br}_2)}{dt} = \frac{k_{\text{II}} I_{\text{abs}}(\text{C}_2\text{H}_2)}{1 + k' / (\text{Br}_2)} \quad 12-7$$

These rate laws may be derived from the following mechanism:



Equation 12-6 is obtained if reaction (7') is the chain terminating step, and equation 12-7 if (7) is the final step. The values of k_{I} , k_{II} , and k' in terms of the constants for the steps in the mechanism are

$$k_{\text{I}} = \frac{2k_4}{k_{7'}}; \quad k_{\text{II}} = \frac{2k_3}{k_{7'}}; \quad k' = \frac{k_6}{k_5}$$

The cause of the change in form of the rate equation with increasing acetylene pressure is apparent if the ratio of the intermediates involved in reactions (7) and (7') is calculated.

$$\frac{(\text{C}_2\text{H}_2\text{Br}_3)}{(\text{Br}_3)} = \frac{k_3(\text{C}_2\text{H}_2)}{k_4 + k_{7'}} \simeq \frac{k_3(\text{C}_2\text{H}_2)}{k_4}$$

The quantum yield measurements show that $k_{7'}$ is negligible as compared to k_4 . According to this equation, high acetylene pressures favor the presence of $\text{C}_2\text{H}_2\text{Br}_3$ and, thus, reaction (7') in preference to (7).

On account of great fluctuations, especially in the dark reaction, Franke and Schumacher²⁹ failed to secure quantitative measurements on the rate of this reaction. It has been pointed out that the variations which they observed are

²⁹ Franke and Schumacher, *Z. physik. Chem.*, **B34**, 181 (1936).

the kind which are usually caused by impurities.³⁰ Insofar as they obtained any information concerning the form of the rate law, the data are in agreement with the equations given by Booher and Rollefson.

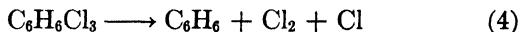
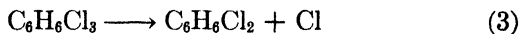
12.45 Addition of the halogens to cyclic compounds.

The reactions of the halogens with the aromatic hydrocarbons are often complicated by the simultaneous occurrence of addition and substitution. Many observations have been published, but the data are not sufficient for a definite determination of the mechanism in any case. The results are illustrated by the work of W. A. Noyes, Jr., and his students, on the chlorination of benzene and the chlorinated benzenes. References to earlier work appear in their papers.

Smith, Noyes, and Hart³¹ studied the reactions between gaseous benzene and chlorine at low pressures. In the initial states of the reaction, practically the only product is $C_6H_6Cl_2$. In the presence of excess chlorine, both addition and substitution occur, yielding C_6Cl_{12} as the ultimate product. A small amount of reaction always occurs in the dark; this is, apparently, exclusively substitution. The rate of the first addition step is in accord with the equation

$$\frac{d(C_6H_6Cl_2)}{dt} = kI_{abs}^{1/2}(Cl_2)(C_6H_6) \quad 12-8$$

This rate law may be derived from the following mechanism:



Reaction (5) requires the presence of a third body to stabilize the Cl_2 molecule, but the experimental data do not extend over a sufficient range to show this effect. Reaction

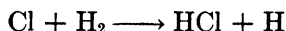
³⁰ Rollefson, *Z. physik. Chem.*, **B37**, 472 (1937).

³¹ Smith, Noyes, and Hart, *J. Am. Chem. Soc.*, **55**, 4444 (1933).

(2) may be reduced to a bimolecular process if it is assumed that the Cl and Cl₂ first form Cl₃. The two possibilities are kinetically identical. The lack of substitution must be due to a higher rate for reaction (2) than for the reaction



Smith, Noyes, and Hart express the opinion that the activation energy of reaction (6) is greater than that for the reaction



If such is the case, the addition of hydrogen to mixtures of benzene and chlorine would tend to suppress the substitution reaction. The activation energy of reaction (2) could be determined by illuminating mixtures of chlorine, hydrogen, and benzene, and determining the relative amounts of C₆H₆Cl₂ and HCl formed.

In mixtures of phenyl chloride and chlorine, the addition and substitution reactions are more nearly comparable, although the latter does not become the predominant reaction until near the end of the reaction. According to the data obtained by Hart and Noyes,³² the ratio of the moles of chlorine substituted to moles added is given by an equation of the form

$$\frac{\text{moles substituted}}{\text{moles added}} = A + k \frac{\text{Cl}_2 \text{ reacted}}{\text{C}_6\text{H}_5\text{Cl initially present}}$$

The thermal reaction, which is appreciable in the experiments at low light intensities, results principally in substitution products. Under comparable conditions at ordinary temperatures, the photochemical rates obtained with phenyl chloride are one-half to one-third those obtained with benzene. The increase in the amount of substitution as compared to addition, which occurs on replacing one hydrogen in benzene with chlorine, indicates that such a replacement lowers the activation energy of the substitution reaction relative to that of the addition reaction.

³² Hart and Noyes, *ibid.*, **56**, 1305 (1934).

Ortho, *meta*, and *para*-dichlorobenzenes all react at approximately the same rate with chlorine.³³ No appreciable thermal reaction occurs, even when the reaction mixtures are allowed to stand for several days. The quantum yields are smaller than for benzene or phenyl chloride under similar conditions. The rate of pressure change (which measures only the addition reaction) is proportional to the pressure of the dichlorobenzene but is independent of the chlorine pressure, except insofar as the amount of radiation absorbed is determined by this quantity. At moderate light intensities, the rate is proportional to the intensity; at high intensities (and also in a larger vessel), the rate depends on some power of the light intensity between 0.5 and 1.0. Fisk and Noyes estimate the activation energy for the chain continuing step $\text{C}_6\text{H}_4\text{Cl}_2 + \text{Cl} \rightarrow \text{C}_6\text{H}_4\text{Cl}_3$ as 5 kcal. per mole. Since this is less than the energy required for the corresponding step in the hydrogen-chlorine reaction, it may be concluded that, if the reaction could be studied at higher pressures, very high quantum yields would be obtained.

³³ Fisk and Noyes, *ibid.*, **58**, 1707 (1936).

CHAPTER XIII

POLYMERIZATION

13.1 Definition. There are many reactions in which is produced a product that is of much higher molecular weight than any of the reactants, that is frequently of unknown or of questionable composition and structure, and that condenses to a liquid or solid at ordinary temperatures. In the photochemical literature such products frequently are loosely described as *polymers*, and the process as *polymerization*.

From a merely practical standpoint such words of loose significance have a certain value, for they allow consideration of a class of reaction which in recent years has acquired great theoretical and technological importance. Originally the subject of polymerization¹ was intended to include only a discussion of those reactions which involve self-addition of like molecules into combinations wherein "primary valence forces are involved." More recently, under the pressure of technological requirement for an omnibus word, a more general definition has been adopted. Polymerization includes the addition of "similar" molecules to each other; it is restricted to the requirement that, by such linkage, a single molecule is formed and that the reactant molecules "must be functionally capable of reacting indefinitely to give molecules of very large size."

It is perhaps true that in most cases the study of photochemical polymerization was not a primary interest. Thus the study of the polymerization of ethylene² followed a study of its reaction with activated hydrogen,³ and our interest in

¹ Cf. Burk, H. E. Thompson, Weith, and I. Williams, *Polymerization*, Reinhold Publishing Corp., New York, 1937, p. 10.

² Olson and Meyers, *J. Am. Chem. Soc.*, **48**, 389 (1926).

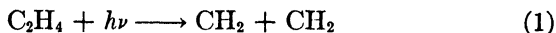
³ Taylor and Marshall, *J. Phys. Chem.*, **29**, 1140 (1925); cf. Berthelot and Gaudechon, *Compt. rend.*, **150**, 1169 (1910).

the polymerization of the aldehydes is secondary to the more extensive study of their photochemical behavior. In the latter case this is so definitely true that we have already discussed the polymerization of the aldehydes *en passant* (§ 8.72). On the other hand, the photochemistry of ethylene and acetylene, for example, has been appropriately reserved for this chapter, even though we have to consider other phases of their behavior.

13.21 Ethylene. Ethylene does not absorb appreciably at wave lengths greater than 2130 Å.⁴ Hilgendorff⁵ identified a number of strong diffuse bands and a series of sharp but weak bands in the region 1973 to 1762 Å. Price⁶ found other diffuse bands beginning at 1744 Å and extending down to 1215 Å. He stated that ethylene (like acetylene) is transparent below 800 Å (at least as far down as 150 Å). There is no specific statement about the range 1215 to 800 Å.

It was found by McDonald and Norrish⁷ that, when ethylene is irradiated at a pressure of less than 1 mm. with light from a hydrogen discharge passed through a fluorite window (i.e., ~ 1250 Å), a polymer is deposited on the window, and hydrogen and some other gas of higher boiling point are formed. This is in agreement with the observation of Mooney and Ludlam that acetylene is formed when C₂H₄ is illuminated with the Al line 1860 Å; McDonald and Norrish favor the idea that the chief constituent of their second fraction is C₂H₂.

The strength of the C=C double bond is 162 kcal.⁸ This corresponds to 1753 Å. Evidently the results of Mooney and Ludlam *cannot* be explained by the primary mechanism



⁴ Mooney and Ludlam, *Trans. Faraday Soc.*, **25**, 442 (1929).

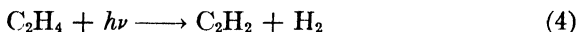
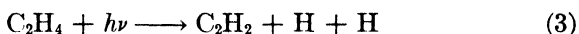
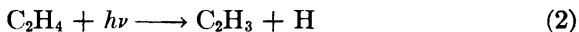
⁵ Hilgendorff, *Z. Physik*, **95**, 781 (1935).

⁶ Price, *Phys. Rev.*, **45**, 843 (1934); *ibid.*, **47**, 444 (1935). Cf. Scheibe and Grieneisen, *Z. physik. Chem.*, **B25**, 52 (1933).

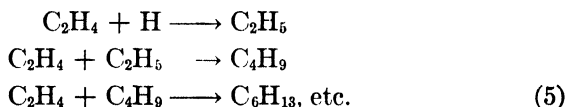
⁷ R. D. McDonald and Norrish, *Proc. Roy. Soc. (London)*, **A157**, 480 (1936). Cf. Mooney and Ludlam, *loc. cit.*; H. S. Taylor and Emeleus, *J. Am. Chem. Soc.*, **53**, 562, 3370 (1931).

⁸ See, however, Appendix II, Table 32.

such as was suggested by Hilgendorff, for at the wave length they used (1860 Å) an insufficient amount of energy is available. The reaction cannot be ruled out as a possibility at the lower wave lengths. However, it has been shown that other primary processes may be considered:



From a consideration of bond strengths it appears that ΔH of reaction (2) is ~ 106 kcal.;⁸ ΔH for reaction (3), according to Tables 30 and 31 (Appendix II), is ~ 146 kcal.; and, accordingly, ΔH for reaction (4) is only ~ 40 kcal. McDonald and Norrish detected no hydrogen atoms either with copper oxide or oxygen. They attribute this result to a rapid reaction between hydrogen atoms and ethylene, and favor the idea that reactions (3) and (4) may compete with each other to an extent determined by the wave length of the light absorbed. The hydrogen atoms from (2) or (3) may, for example, combine with C_2H_4 to give C_2H_5 , which might then enter into many addition reactions:



By treating pure C_2H_2 under the same conditions as had been used for C_2H_4 , McDonald and Norrish showed that the amount of polymer formed could not be accounted for by an intermediate process involving acetylene. They found that, although there was a measurable decrease in pressure, it was too slow to be a contributing factor in the ethylene polymerization. These experiments do not exclude the possibility that the atoms or radicals formed by the action of light on C_2H_4 can catalyze the polymerization of C_2H_2 to a rate greater than that in the pure substance.

The conclusions expressed by McDonald and Norrish are in agreement with the results obtained by O. K. Rice

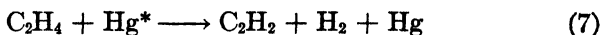
and Sickman,⁹ and by Taylor and his co-workers. The former showed that the polymerization of ethylene may be induced at 290° and 300° by free methyl radicals produced by the pyrolysis of azomethane (cf. § 8.32). Taylor and Jungers¹⁰ performed even more convincing experiments in which the ethylene was polymerized at room temperature by methyl radicals liberated by the photolysis of acetone. Many years earlier Taylor and Jones¹¹ had induced polymerization of ethylene by free ethyl radicals produced from the pyrolysis of mercury diethyl and lead tetraethyl.

Of course, the best proof for the mechanism suggested for the photolysis and resultant polymerization of ethylene would be a direct detection of free radicals produced in the primary steps. Mirror methods (cf. § 5.91) might be used.

Olson and Meyers² found that, when a mixture of ethylene and hydrogen containing mercury vapor is exposed to the mercury resonance line 2537 Å, the reaction does not go smoothly to form ethane by the overall reaction



but the ethylene itself is polymerized, there being an initial increase in pressure which falls off again as the polymerization proceeds. This result was verified by Bates and Taylor,¹² who suggested the primary reaction



That this reaction does occur to some extent was proved by passing the gases into a solution of ammoniacal cuprous chloride; copper acetylide was precipitated. However, we have already seen, from the work of McDonald and Norrish, that the intermediate formation of C_2H_2 cannot by itself

⁹ O. K. Rice and Sickman, *J. Am. Chem. Soc.*, **57**, 1384 (1935); Sickman and Rice, *J. Chem. Phys.*, **4**, 608 (1936).

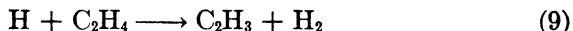
¹⁰ Taylor and Jungers, *Trans. Faraday Soc.*, **33**, 1353 (1937). Cf. Taylor and Emeleus, *J. Am. Chem. Soc.*, **53**, 562 (1931), who caused polymerization of C_2H_4 with H atoms from photolysis of NH_3 .

¹¹ Taylor and W. H. Jones, Jr., *J. Am. Chem. Soc.*, **52**, 1111 (1930). Cf. Cramer, *ibid.*, **56**, 1234 (1934), for similar work in benzene solution.

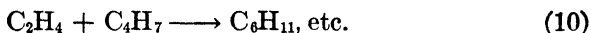
¹² Bates and Taylor, *ibid.*, **49**, 2438 (1927).

account for the amount of polymer formed. The reaction analogous to (3) is evidently barred on energetic grounds.

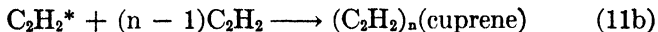
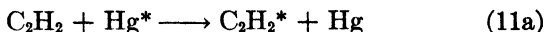
A clue to a possible primary process is afforded by the experiments of Klemenc and Patat.¹³ They found that, when hydrogen atoms produced either by excited mercury atoms or by an electrical discharge (see § 10.31) were permitted to act on ethylene, acetylene was formed. It was concluded that hydrogen atoms could dehydrogenate, as well as hydrogenate, ethylene. The observed formation of H₂ might also be accounted for by the successive reactions:



Any H atoms formed would be expected to disappear either as indicated above or by addition to a C₂H₄ molecule to yield C₂H₅; because of the much larger probability of reactions involving C₂H₄, they would not be expected to yield H₂ by a three-body collision with another H atom. The C₂H₃ radicals might now lead to polymer formation in much the same way as suggested by McDonald and Norrish for C₂H₅; i.e.,



Of course, the conditions of the photosensitized process are not precisely the same as those of the straight photochemical process. It is altogether possible that C₂H₂ formed in such a reaction as (7) might account for polymer formation via other reactions suggested; namely,



Olson and Meyers,¹⁴ using mass spectrographic methods of analysis,¹⁵ concluded as a result of their experiments that

¹³ Klemenc and Patat, *Z. physik. Chem.*, **B3**, 289 (1929).

¹⁴ Olson and Meyers, *J. Am. Chem. Soc.*, **49**, 3131 (1927).

¹⁵ Unfortunately, as pointed out by H. R. Stewart and Olson, *ibid.*, **53**, 1236 (1931), the precise products and concentrations indicated by the analyses are not to be given too much weight. More extensive study shows that new molecules and radicals might be created in the ion stream of the mass spectrograph.

there might be a third process analogous to reaction (1). However, inasmuch as the Hg^* atom can provide only ~ 112 kcal., this reaction seems unlikely. Other reactions which they suggested, involving CH_2 radicals, C_2H_4 molecules, and H atoms building up into larger molecules, are of the form that might be expected.

The first resonance line of cadmium lies at $3262 \text{ \AA}$., corresponding to ~ 87 kcal. per mole. Bates and Taylor¹⁶ found that, although a mixture of ethylene and hydrogen containing cadmium vapor is unaffected on prolonged standing at 255° to 260° , exposure to the resonance line causes a notable diminution in pressure. On the other hand, it was found later by Jungers and Taylor¹⁷ that the sodium resonance lines ($\lambda\lambda = 5896 \text{ \AA}$ and $5890 \text{ \AA} \approx 48$ kcal. per mole) acting on ethylene containing sodium vapor were not similarly effective at 132° to 255° , even though the sodium fluorescence was completely quenched.

As for the cadmium reaction, formation of H atoms from H_2 cannot be the primary process. The heat of formation of H_2 is ~ 103 kcal., about 16 kcal. in excess of that available from the excited Cd (5^3P_1) atom. Simple calculation (see § 5.21) shows that, at the temperature of the experiment, less than one in 10^6 collisions between a H_2 molecule and an excited Cd atom would yield a hydrogen atom. The data presented by Bates and Taylor are insufficient to draw any further conclusions as to the possible primary reaction between Cd^* and C_2H_4 . However, in view of the result obtained with Na^* and the theoretical significance of the possible results, it seems that the experiments involving excited Cd merit careful repetition and extension.

Attention has been called to a conclusion from theory (see §10.31) that the best possible condition for a collision of the second kind is one in which a minimum amount of energy is converted into kinetic energy. Reaction (4), producing a hydrogen molecule, requires at least 45 kcal., and, since the excited Na ($^2P_{1/2, 3/2}$) atom furnishes 48 kcal., it might be

¹⁶ Bates and Taylor, *ibid.*, **50**, 771 (1928).

¹⁷ Jungers and Taylor, *J. Chem. Phys.*, **4**, 94 (1936).

presumed to be particularly effective in sensitizing that reaction. The failure of Na^* to produce any chemical effect, in spite of the fact that its fluorescence is completely quenched by C_2H_4 , merely indicates that the energy of activation of reaction (4) is considerably in excess of the minimum calculated from heat of combustion data. It is interesting in this connection to note that the energy of activation of the polymerization of ethylene, determined thermally,¹⁸ is 35 to 42 kcal.

Data on the polymerization of some other alkenes and alkene derivatives are included in Table 22.

TABLE 22
DATA ON POLYMERIZATION OF SOME ETHYLENE AND
ACETYLENE DERIVATIVES, ETC.

Substance	Formula	λ , Å	γ (approx.)	Reference
Styrene.....	$\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$	4000–3000 ^a	2	(1), (2)
Vinyl acetate.....	$\text{CH}_3\text{COOCH}=\text{CH}_2$	4000–3000 ^a	550	(1), (2)
Methyl acetylene	$\text{CH}_3\text{C}\equiv\text{CH}$	2200	3.5	(3)
Allene.....	$\text{H}_2\text{C}=\text{C}=\text{CH}_2$	2300	2.5	(3)
Butadiene.....	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	< 2300	—	(4)
Isoprene.....	$\text{CH}_2=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}_2$	Hot Hg arc	—	(3)
Cyclopropane.....	C_3H_6	$\text{Hg}^*(2537)$	—	(5)
Methyl metacrylate.....	$\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_3$	> 2200 ^b	—	(6)

^a Shorter wave lengths decrease the quantum yield presumably by decomposing the polymer.

^b Light of < 2200 causes decomposition.

REFERENCES

- (1) Taylor and Vernon, *J. Am. Chem. Soc.*, **53**, 2527 (1931).
- (2) Jeu and Alyea, *ibid.*, **55**, 575 (1933).
- (3) Lind and Livingston, *ibid.*, **55**, 1036 (1933).
- (4) Kublitskii, *Sintet. Kauchuk* (U.S.S.R.), **1936**, No. 7–8, pp. 30–32.
- (5) Harris, Ashdown, and Armstrong, *J. Am. Chem. Soc.*, **58**, 852 (1936).
- (6) Melville, *Proc. Roy. Soc. (London)*, **A163**, 511 (1937).

13.22 Acetylene. According to Kistiakowsky,¹⁹ pure acetylene is completely transparent down to 2400 Å. At

¹⁸ Pease, *J. Am. Chem. Soc.*, **53**, 613 (1931); Storch, *ibid.*, **56**, 374 (1934).

¹⁹ Kistiakowsky, *Phys. Rev.*, **37**, 276 (1931).

atmospheric pressure, beginning at $\sim 2377 \text{ \AA}$ ($42,056 \text{ cm.}^{-1}$) and extending to $\sim 2246 \text{ \AA}$ ($44,514 \text{ cm.}^{-1}$), a number of bands (some extremely faint) were noted. There was distinct evidence of structure. The difficulty of observation was enhanced by a continuous background which set in at ~ 2350 to $2300 \text{ \AA}$ and became quite strong below $2250 \text{ \AA}$.

Since Stark and Lipp²⁰ were able to observe absorption bands down to $1900 \text{ \AA}$, Kistiakowsky suggested that the continuum which he observed was probably due to the presence of impurities. This surmise was later supported by Dieke,²¹ who showed that even around $1900 \text{ \AA}$ he could observe bands which showed a distinct structure. Price²² found another extensive system of bands in the range 1520 to $1050 \text{ \AA}$ ²³ at acetylene pressures of 0.1 mm. or less. Unlike the bands at the higher wave lengths, the bands around $1500 \text{ \AA}$ are very diffuse. At $1350 \text{ \AA}$, they are less diffuse; below that wave length, they become sharp again. At the shorter wave lengths, they become very numerous and overlap, reaching a limit at $\sim 1050 \text{ \AA}$ (11.75 e.v.), where continuous absorption starts. This becomes rapidly weaker and disappears at $\sim 800 \text{ \AA}$. Like ethylene the gas is transparent thereafter, at least down to $150 \text{ \AA}$. Price calculated a Rydberg series from his data for acetylene, and from the series limit calculated the ionization potential to be at $11.35 \pm 0.01 \text{ e.v.}$ This is in close agreement with the determination by Tate and Smith,²⁴ who obtained a value of $11.6 \pm 0.1 \text{ e.v.}$ by the method of electron impact.

Price analyzed the absorption spectrum of acetylene and was able to translate his results, in part, into the potential energy diagram for the $\text{C}\equiv\text{C}$ link shown in Fig. 50. According to this analysis, the bands observed by Kistiakowsky are probably due to the electronic transition from the unexcited curve n to the curve K . The n and K curves have the

²⁰ Stark and Lipp, *Z. physik. Chem.*, **86**, 36 (1913).

²¹ Cf. Price, *Phys. Rev.*, **47**, 444 (1935).

²² Price, *Phys. Rev.*, **45**, 843 (1934); *ibid.*, **47**, 444 (1935). Price also measured the absorption of C_2D_2 .

²³ Cf. Herzberg, *Trans. Faraday Soc.*, **27**, 378 (1931).

²⁴ Tate and P. T. Smith, *Phys. Rev.*, **39**, 270 (1932).

same limit at slightly less than 8.1 e.v.; i.e., slightly less than 187 kcal. Since this cannot correspond to the strength of the C—H bond, it must be the limiting value for the strength of

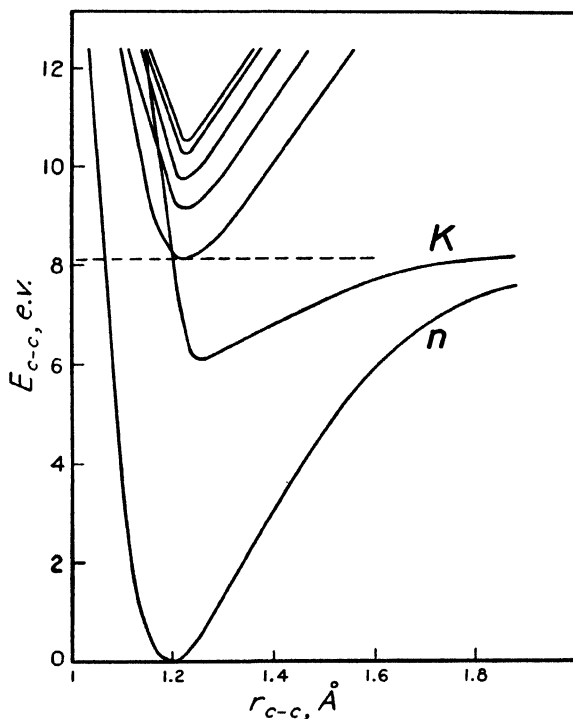


Fig. 50. Potential Energy Diagram for the C≡C Link in Acetylene, according to Price, *Phys. Rev.*, **47**, 444 (1935). Cf. Hankin and Burton, *J. Chem. Phys.*, **8**, 297 (1940), and forthcoming publication.

the C≡C bond; i.e., the predissociation limit at 1520 Å corresponds very closely to the strength of the C≡C bond.²⁵ This value may be compared with the calculated values of 200 kcal. given by Pauling²⁶ and of 220.5 kcal. given by Norrish.²⁷ The sharpness of the *Kistiakowsky bands*, the

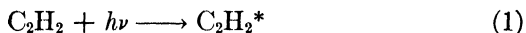
²⁵ This close correspondence of predissociation limits to particular bond strengths frequently occurs in the case of polyatomic molecules. The theory involved is discussed in § 4.3 et seq.

²⁶ Pauling, *J. Am. Chem. Soc.*, **54**, 3570 (1932).

²⁷ Norrish, *Trans. Faraday Soc.*, **30**, 103 (1934).

diffuseness at $\sim 1500 \text{ \AA}$, and the sharpening beyond $1350 \text{ \AA}$ are explained by this potential energy diagram. The ionization potential at 11.35 volts does not appear on the diagram, which relates only to the $\text{C}\equiv\text{C}$ bond.

The photochemical information on acetylene is most meager. No decomposition has been reported, for the very obvious reason that the investigators did not work at sufficiently low wave lengths (i.e., $< 1520 \text{ \AA}$). Acetylene is known to polymerize into a deep yellow compound, probably cuprene,²⁸ with a quantum yield reported by Lind and Livingston to be 9.2 ± 1.5 at an average wave length of $2150 \text{ \AA}$. The 10° temperature coefficient of the quantum yield is stated to be 1.25. Light of $2537 \text{ \AA}$ or longer was shown to be ineffective. At the lower end, the apparatus transmitted only down to $2050 \text{ \AA}$. Since absorption is discrete down to that point, it is apparent that the polymerization reaction may involve excited acetylene molecules, the first step being



Sickman and Rice²⁹ state that methyl radicals from azomethane cause the polymerization of acetylene; Taylor and Jungers³⁰ have shown that methyl radicals from the photolysis of acetone have the same effect. Consequently it may be presumed that the high quantum yield of photochemical polymerization of pure acetylene is due to the formation of free radicals or atoms in a secondary step. However, it is noteworthy, in contradiction to such an assumption, that Melville³¹ failed to find any trace of either hydrogen or methane among the products of acetylene subjected to mercury-sensitized polymerization (cf. ethylene,

²⁸ Berthelot and Gaudechon, *Compt. rend.*, **155**, 207 (1912). Bates and Taylor, *J. Am. Chem. Soc.*, **49**, 2438 (1927). Reincke, *Z. angew. Chem.*, **41**, 1144 (1928). Lind and Livingston, *J. Am. Chem. Soc.*, **52**, 4613 (1930); **54**, 94 (1932).

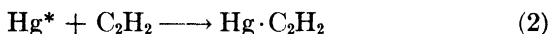
²⁹ Sickman and O. K. Rice, *J. Chem. Phys.*, **4**, 608 (1936).

³⁰ Taylor and Jungers, *Trans. Faraday Soc.*, **33**, 1353 (1937). Cf. *J. Chem. Phys.*, **3**, 338 (1935), for studies by the same authors of photosensitized decomposition of C_2H_2 and C_2D_2 .

³¹ Melville, *Trans. Faraday Soc.*, **32**, 258 (1936).

§ 13.21). Furthermore, Kemula and Mzrazek ³² have detected traces of benzene spectroscopically during the photochemical polymerization of acetylene at room temperature, and Livingston and Schifflett ³³ have obtained isolable quantities on prolonged illumination at 175° to 250°.

To explain his observations with the mercury-photo-sensitized reaction, Melville ³¹ suggested that the excited mercury atom forms a complex with an acetylene molecule



and that such a complex may then add on further acetylene molecules, thereby producing a polymer by a chain mechanism. The chain length (i.e., the number of C_2H_2 molecules polymerized per excited Hg atom deactivated by C_2H_2) increases from 10 at 20° to 100 at 250°, and thereafter decreases. According to Melville, the kinetics of the process are consistent with the assumption that the cessation of the growth of the polymer is due "to a collision of an acetylene molecule with the growing polymer but of a different kind to that responsible for propagation."

Melville also offered the interesting suggestion (cf. § 13.21) that polymerization of ethylene may be due to a similar phenomenon, with the acetylene formed in the first stage polymerizing as indicated, and ending with the hydrogenation of the acetylene polymer.

Beyond the proposal of Melville, which is intended to apply to the mercury-sensitized reaction, and the suggestion based on the work of Sickman and Rice ²⁹ and of Taylor and Jungers ³⁰ that the high quantum yield may be due to free radicals or atoms formed in a secondary step, little can be said of the mechanism of the polymerization of acetylene.

Data on methyl acetylene is included in Table 22.

³² Kemula and Mzrazek, *Z. physik. Chem.*, **B23**, 350 (1934). Cf. Toul, *Collection Czechoslov. Chem. Communications*, **7**, 491 (1935); Kemula, *ibid.*, **7**, 493 (1935).

³³ Livingston and Schifflett, *J. Phys. Chem.*, **38**, 377 (1934). Cf. Mund and Rosenblum, *ibid.*, **41**, 369 (1937), who induced polymerization with α , β , and γ rays with similar results.

13.3 Anthracene. The stable form of anthracene is the monomer. When solutions of the monomer are exposed to ultraviolet light, the unstable dimer is produced.³⁴ In the dark the reaction reverses until, at equilibrium, the solute consists almost exclusively of the monomer:



The concentration of the dimer in the photostationary state and the influence of such factors as temperature,³⁵ concentration,³⁶ and solvent³⁷ have been repeatedly studied. On illumination, the solutions show electrical conductivity.³⁸

At the present time there is no evidence to indicate whether or not the fluorescence, polymerization, and electrical conductivity occur on illumination in the same spectral region, or whether the same primary process is involved in every case. However, as Bonhoeffer and Harteck³⁹ point out, it is unlikely that the amount of energy available in the absorbed light quantum would be sufficient for ionization; the conductivity probably results from the accumulation of energy in some other way (perhaps by a secondary process).

The corresponding polymerization of methylanthracene has also been studied.⁴⁰ The mechanism of the photodimerization of these compounds, as well as others, has been discussed by Schönberg,⁴¹ who assumed the intermediate formation of a biradical; e.g., in the case of anthracene, the primary reaction is presumed to be

³⁴ Other cases of the production of the unstable isomer by the agency of light are the *cis-trans* reactions already described (§§ 9.2 to 9.22).

³⁵ Luther and Weigert, *Z. physik. Chem.*, **51**, 397 (1905); **53**, 385 (1905).

³⁶ See also Byk, *ibid.*, **62**, 454 (1908); *Z. Elektrochem.*, **14**, 460 (1908); Weigert, *Z. physik. Chem.*, **63**, 458 (1908).

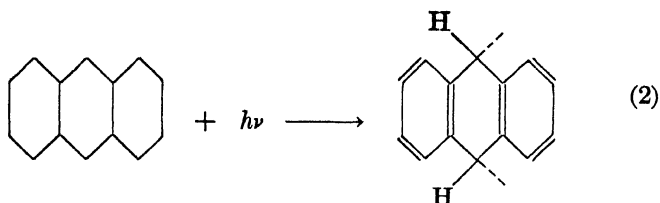
³⁷ Cf. Lauer and Oda, *Ber.*, **69B**, 137 (1936).

³⁸ Volmer, *Ann. Physik*, **40**, 775 (1913); Volmer and Riggert, *Z. physik. Chem.*, **100**, 502 (1922).

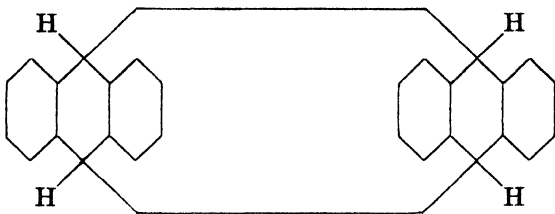
³⁹ Bonhoeffer and Harteck, *Grundlagen der Photochemie*, Theodor Steinkopff, Dresden, 1933, p. 169.

⁴⁰ Weigert and Kruger, *Z. physik. Chem.*, **85**, 579 (1913).

⁴¹ Cf. Schönberg, *Trans. Faraday Soc.*, **32**, 514 (1936).

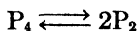


Two radicals formed, as by reaction (2), may then combine to give



The quantum yield of 0.48, reported by Weigert ⁴² for high anthracene concentrations in benzene, toluene, and xylene at 3650 and 3130 Å, is in agreement with such a mechanism, but L. Farkas (private communication) has found that, contrary to what might be expected for a biradical mechanism, the rate of the para-ortho hydrogen conversion is not increased in illuminated solutions of anthracene.

13.4 Phosphorus. Of the two allotropic modifications of phosphorus, the red form is usually regarded as a polymer.⁴³ Ordinarily the interchange of these forms has been studied thermally. However, Rathenau ⁴⁴ has found that, when a solution of P_4 in carbon disulfide is illuminated in the near-ultraviolet, conversion to the red form occurs via a unimolecular reaction. The first stage is believed to be



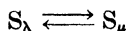
The P_2 molecules combine to give red phosphorus.

⁴² Weigert, *Naturwissenschaften*, **15**, 124 (1927).

⁴³ Cf. Melville and S. C. Gray, *Trans. Faraday Soc.*, **32**, 271 (1936); Norrish, *ibid.*, **32**, 285 (1936); Melville, *ibid.*, **32**, 286 (1936).

⁴⁴ Rathenau, *Physica*, **4**, 503 (1937).

13.5 Sulfur. We may discuss at this point the rearrangement of sulfur:



The latter is the colloidal, insoluble modification and is presumed to consist of molecules composed of long chains of atoms. S_{μ} is thermally unstable and rearranges to S_{λ} . At low temperature the equilibrium is distinctly in favor of S_{λ} . When solutions of S_{λ} in CS_2 , CCl_4 , or C_6H_6 are illuminated by blue or violet light, S_{μ} is formed.⁴⁵ In the dark the reaction reverses.

13.6 Aldehydes. As we have already seen (§ 8.72), polymerization of the aldehydes incidentally to their photolysis introduces complexities into the study of the latter. The polymerization can be of two kinds: it may be addition of like molecules; or it may be the result of the reaction between an unchanged molecule and a fragment produced in the photolysis, as in the case of the unsaturated aldehydes.⁴⁶ Although there is reason to believe that the polymerization of acetaldehyde may proceed by the first mechanism,⁴⁷ Blacet and Volman⁴⁸ have found evidence for the latter process in that case.

One of the commonly considered theories of photosynthesis is that formaldehyde is formed in a primary process and that this compound polymerizes to a sugar. The polymerization of $HCHO$ by ordinary chemical means is well known. Dhar and his co-workers⁴⁹ claim that the formation of a reducible sugar is accelerated by light and ferric salts. According to Baly, Heilbron, and Barker,⁵⁰ sugar is formed from a solution of formaldehyde exposed to ultraviolet light in the presence of calcium carbonate; the optimum temperature is said to be 37°.

⁴⁵ Wigand, *Z. physik. Chem.*, **77**, 423 (1911); *Ann. Physik*, **29**, 1 (1911).

⁴⁶ Thompson and Linnett, *J. Chem. Soc.*, 1452 (1935); Blacet, Young, and Roof, *J. Am. Chem. Soc.*, **59**, 608 (1937); Blacet, Fielding, and Roof, *ibid.*, **59**, 2375 (1937).

⁴⁷ Cf. Rollefson, *J. Phys. Chem.*, **41**, 259 (1937); Burton, *ibid.*, **41**, 322 (1937).

⁴⁸ Blacet and Volman, *J. Am. Chem. Soc.*, **60**, 1243 (1938).

⁴⁹ N. R. Dhar, *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 151 (1935); Ram and Dhar, *J. Indian Chem. Soc.*, **14**, 151 (1937).

⁵⁰ Baly, Heilbron, and Barker, *J. Chem. Soc.*, **119**, 1025 (1921); Baly, *Ind. Eng. Chem.*, **16**, 1016 (1924).

CHAPTER XIV

EFFECTS IN THE LIQUID STATE

14.1 General effects. Several reactions which have been studied in solution or in the liquid phase have already been discussed. In such cases either no new phenomena have been introduced in the condensed phase or what alterations have been produced have been dealt with at those points. In this chapter our interest is not in all photochemical studies that have been conducted in the liquid phase. Instead, we address ourselves only to major effects which may be expected in condensed systems and select from the overwhelming mass of experimental data only a relatively few experiments that are well suited to the purposes of illustration.

14.11 Franck-Rabinowitch hypothesis. In a gas at atmospheric pressure and $0^{\circ}\text{C}.$, the mean free time of a molecule is of the order of 10^{-10} sec. If the lifetime of the excited state is of the order of 10^{-13} sec., as it is in a simple rupture process (cf. § 4.3), it is obvious that the yield of the primary reaction will not be substantially affected by neighboring molecules. On the other hand, in a liquid the conditions are quite different. Conditions of collision, in which a solvent molecule is a second or third body, are always present; hence we may speak of the mean free time of the molecule or of its decomposition products as being of the order of 10^{-13} sec., or less. It is interesting to examine the significance of this conclusion in relation to the quantum yield in the liquid state.

In the discussion in this section it will be convenient to neglect the possibility of fluorescence, since it has no bearing on the nature of our results and since, further, it does not actually occur in most of the cases with which we are

concerned. It will be assumed that a molecule loses its absorbed energy only by collision or by decomposition. Franck and Rabinowitch¹ suggested that, under such conditions, the actual quantum yield of the product observed would be modified in the liquid state.

If the excited molecule collides with a molecule of the solvent before decomposition occurs, there is a probability of dissipation of the energy. In the study of the quenching of fluorescence in gases, it has been found that practically every collision with a complex molecule is effective (cf. § 3.35). The molecules of the solvents used in photochemical reactions are usually sufficiently complicated that the possibility of a high efficiency of the deactivation process must be considered. The fact that the absorbed energy is not always lost in this way is demonstrated by the existence of many examples of fluorescence in solution. The solute molecules in such cases are much more complex than those which have been used in the gas phase studies, and the increased stability toward collisions is probably due to this complexity. If the energy absorbed by the solute molecule is transferred to a solvent molecule, the latter molecule is raised to a higher level, from which it is in turn deactivated by other solvent molecules. In this way the absorbed energy may be dissipated without causing any chemical reaction.

A second way for dissipating the energy may be chemical reaction between the activated molecule and the solvent. Franck and Rabinowitch suggest, for example, that an excited Br_2 molecule (possessing about 4 volts activation energy) may react with a solvent molecule (such as CCl_4) to give CCl_3Br and ClBr ; or CCl_3 , ClBr , and Br ; or even simple dissociation into CCl_3 and Cl . Such a reaction would reverse in the dark, and the quantum yield would be nil. This mechanism is not supported by a direct test made by Rollefson and Libby,² who studied the chemically simple case of radioactive Cl_2 dissolved in CCl_4 . On the basis of the above suggestion, it would be expected that illumination of

¹ Franck and Rabinowitch, *Trans. Faraday Soc.*, **30**, 120 (1934).

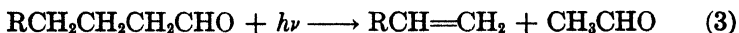
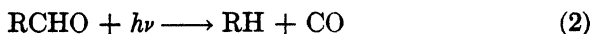
² Rollefson and Libby, *J. Chem. Phys.*, **5**, 569 (1937).

the solution with a quartz mercury arc would lead to some chlorine exchange. No such effect was detected.

However, there are cases in which reaction between the excited molecules or resultant atoms and the solvent molecules may occur in an *irreversible* process. Attention is called to an experiment³ on the photobromination of benzene in the liquid state and in CCl_4 solution, in which both $\text{C}_6\text{H}_5\text{Br}$ and $\text{C}_6\text{H}_6\text{Br}_6$ were obtained. Rabinowitch attributed the former to short chain reactions in which the primary dissociation into Br atoms leads to a substitution, and the latter to addition of activated Br_2 molecules to the C_6H_6 . According to this idea, study of this reaction in the gaseous phase in the region of the Br_2 continuum should lead to $\text{C}_6\text{H}_5\text{Br}$ as the chief bromination product.

Even though the energy of a molecule may not be dissipated before decomposition, there is another factor peculiar to liquids which may cut down the yield. There is always the possibility that the products of the primary decomposition may lose all their energy by collision while they are still within each other's spheres of influence. If a solution is involved, this is more likely to be the case the larger the molecules of solvent and the primary particles formed. Thus, there is a possibility that H atoms may penetrate a sheath of solvent molecules without collision; however, when radicals are produced by the photolysis, the chance of such escape is decreased, particularly when the solvent itself is of high molecular weight. A good illustration of this phenomenon is afforded by the photolysis of aldehydes and ketones in the liquid state and in solution.

14.12 Aldehydes and ketones. Aldehydes and ketones in the vapor state may decompose in several ways, depending upon the lengths of the alkyl radicals (cf. §§ 8.72, 8.76). The various possible overall primary processes for the aldehydes are:



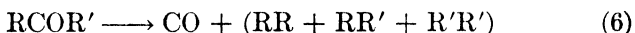
³ Rabinowitch, *Z. physik. Chem.*, **B19**, 190 (1932).

For the ketones, only the following reactions occur as primary overall processes:⁴



The radical $\text{R}'\text{CO}$ formed in reaction (4) is quite stable at room temperature. However, as the temperature is increased, its stability is decreased; at 60° , the radical CH_3CO is quite unstable. On the other hand, the radical HCO is stable even at temperatures up to 100° .

The results obtained on photolysis of aldehydes and ketones in the liquid state and in a non-polar solvent are in consonance with what might be expected on the basis of the Franck-Rabinowitch hypothesis.⁵ It has been found, for example, that methyl ethyl ketone and ethyl ketone in 10 per cent liquid paraffin solution show no yield of gaseous products at 20° but decompose according to the overall reaction



at 100° . This result indicates that, for these ketones, the primary reaction is exclusively (4); i.e., a free radical process is involved. Collision with the solvent occurs while the product radicals are still within each other's spheres of influence, and either recombination or reaction with the solvent takes place. However, at higher temperatures the radical $\text{R}'\text{CO}$ is known to be unstable. It is possible that at such temperatures the $\text{R}'\text{CO}$ is formed with so much energy that it immediately decomposes (cf. HgH § 3.34), and hence the primary process is essentially



⁴ In this summary we neglect consideration of activation as a separate process. Reactions (3) and (5) are established in those cases where R is a hydrogen atom.

⁵ (a) Norrish and Bamford, *Nature*, **140**, 195 (1937); cf. *ibid.*, **138**, 1016 (1936). (b) Norrish, *Trans. Faraday Soc.*, **33**, 1521 (1937). (c) Earlier similar results of Bowen and his co-workers, *J. Chem. Soc.*, 1503, 1505 (1934); *ibid.*, 1685 (1936), with pure liquid aldehydes and ketones, as well as in solution, may also be interpreted according to the Franck-Rabinowitch ideas. (d) Cf. § 8.72 for photolyses of aldehydes in aqueous solution.

where CO is a stable molecule. Under these conditions, recombination of the radicals produced in reaction (4) does not occur.

Di-*n*-propyl ketone contains alkyl radicals sufficiently long for the photolysis to proceed via the mechanism of reaction (5). This is actually observed in the vapor state, and the quantum yield of this reaction remains the same (i.e., ~ 0.3) when the photolysis is conducted in *iso*-octane solution. However, although di-*n*-propyl ketone also decomposes via reaction (6) with a quantum yield of ~ 0.23 in the vapor state, the quantum yield of that reaction in the same solution at 20.5° is cut to ~ 0.01 .^{5b} According to Norrish, the two results are also to be expected on the basis of the Franck-Rabinowitch hypothesis. Only that reaction proceeds in solution at ordinary temperatures which results in the formation of stable molecules in the primary act. When free radicals are formed, they recombine (or react with the solvent) as a result of the first collision process.

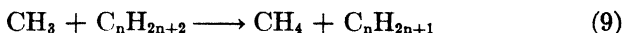
This conclusion may be used to interpret a further result of Norrish and Bamford.^{5a} They found that aldehydes are photolyzed in solution at room temperature, yielding the same gaseous products in solution as in the gas phase. In the case of acetaldehyde a slight excess of CH₄ over CO in the solution reaction is attributed to the formation of a small amount of CH₃, which reacts with the solvent



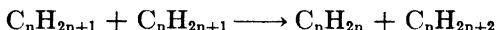
while the HCO radical is simultaneously removed without the production of CO. The photolysis of CH₃CHO in solution, with practically undiminished yield, is then to be attributed to the fact that most of the photolysis probably proceeds via the formation of ultimate molecules in the primary step; i.e., via reaction (2). When aldehydes such as butyl and valeryl aldehydes are studied, there is equally good evidence for the absence of reaction (1) and the simultaneous occurrence of reactions (2) and (3).

An interesting point developed by Norrish^{5b} is that, in

cases where free radicals are actually produced in solution (e.g., in the photolysis of ketones), there is evidence for reactions of the type



Subsequently, unsaturated molecules are produced in the solvent by the disproportionation reaction



and this unsaturation may actually be measured by titration with bromine water.

The results of Bamford and Norrish, and of Bowen and his co-workers,^{5c} are perhaps the best evidence available at the present time in support of the views of Franck and Rabinowitch.

14.13 Other evidence concerning the Franck-Rabinowitch hypothesis. Dickinson⁶ tabulated many reactions which proceed both in the gas and in the liquid phase or in solution, and which possess the common characteristic that they either have "about the same quantum yield or the same specific rate in each, or else proceed more rapidly in the gas."

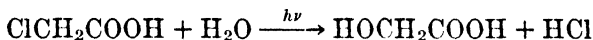
Parts of this list with some modifications are quoted in Table 23 (pp. 362-363). The reduction of quantum yields in the liquid or solution may be caused either by some such mechanism as proposed by Franck and Rabinowitch or by a chain-breaking mechanism. The latter mechanism is improbable in cases where the quantum yield in the gaseous state is less than unity. In certain cases (e.g., ClO_2 in water), there is an interaction of the products with the solvent. Some of the reactions are discussed more extensively elsewhere, as noted in the table.

14.14 Photohydrolysis of monochloroacetic acid. The quantum yield of this reaction has been studied repeatedly,⁷ perhaps because of its evident desirability as a

⁶ Dickinson, *Chem. Rev.*, **17**, 413 (1935).

⁷ (a) Rudberg, *Z. Physik*, **24**, 247 (1924). (b) L. Farkas, *Z. physik. Chem.*, **B23**, 89 (1933). (c) R. N. Smith, Leighton, and Leighton, *J. Am. Chem. Soc.*, **61**, 2299 (1939). (d) Thomas, *ibid.*, **62**, 1879 (1940).

chemical actinometer.^{7b,8} Until recently, it was thought that the quantum yield was unity,^{7a} a value abnormally high for a simple reaction in the liquid state. However, Smith, Leighton, and Leighton,^{7c} and Thomas^{7d} have recently shown that for the over-all reaction



the quantum yield at 2537 Å varies from 0.31 at 25° to 0.69 at 69°. A somewhat lower (corrected) value of 0.11 has been reported for the quantum efficiency of the bromoacetic acid photohydrolysis.^{7a}

14.15 Alkyl iodides. The quantum yield of the photolysis of ethyl iodide vapor is < 0.01 in the region of continuous absorption (i.e., at ~ 2500 Å). In the liquid state, however, it is 0.41 at 2537 Å.⁹ This increase over the quantum yield in the gaseous state is the opposite of what might be expected on the basis of the Franck-Rabinowitch hypothesis (cf. § 14.11). It has been suggested¹⁰ that the iodine production may be due to the presence of air or moisture.¹¹ However, this explanation is not necessary to the interpretation of the result.

Rollefson and Libby³ have pointed out that, in the usual photodissociation, the parts separate from each other with abnormally high kinetic energies and with a consequently increased probability of forcing their way between the solvent molecules. Hence the primary recombination effect postulated by Franck and Rabinowitch might not be an influential factor in a case such as this, where one of the product particles is an atom and the surrounding molecules are not particularly large. In the vapor state the quantum yield is cut down by virtue of the fact that the combination of ethyl radicals seems to require a three-body collision,

⁸ Dain and Pusenkin, *Ber. ukrain. wiss. Forsch.-Inst. physik. Chem.*, **4**, 75 (1934).

⁹ Norton, *J. Am. Chem. Soc.*, **56**, 2294 (1934).

¹⁰ Dickinson, *Chem. Rev.*, **17**, 413 (1935).

¹¹ Cf. Stobbe and Schmitt, *Z. wiss. Phot.*, **20**, 57 (1920).

TABLE 23

QUANTUM YIELDS OF SOME REACTIONS IN GASEOUS
AND CONDENSED SYSTEMS

(Cf. §§ 14.1 to 14.13.)

Reaction	Wave Length Å	QUANTUM YIELDS			Reference
		Gas	CCl ₄		
NO ₂ → NO + ½ O ₂	4358	0	0.03 0.02 (0.15)		(1)
	4050	0.50			
	3660	1.83			
	3130	1.93			
N ₂ O ₅ → 2NO + ½ O ₂	2800	0.6	0.04		(1)
	2650	0.6	0.05		
Cl ₂ O → Cl ₂ + ½ O ₂ (also ClO ₂)	4358	3.2	1.8		(2-4)
	3650	3.4			
	3130	3.5			
	2537	4.5			
ClO ₂ → ½ Cl ₂ + O ₂	4358 4050 3665 3650 3130 3000	Gas	CCl ₄	Water	(5-8), (22)
		Much ClO ₃ formed; chains.	1.0	0.20	
			2.2	0.50	
			2.0	0.76	
			2.0		
			2.1	1.0	
Pb (CH ₃) ₄ → Pb + 2C ₂ H ₆	2537	Gas	Hexane		(9)
		1.1	0.4		
2Fe (CO) ₅ → Fe ₂ (CO) ₉ + CO	4358 4050 3660 3000 2540	Gas	Liquid		(10-12)
		2.32	1.66		
			1.76		
			1.86		
			1.89		

REFERENCES

- (1) Holmes and Daniels, *J. Am. Chem. Soc.*, **56**, 630 (1934).
- (2) Finkelnburg, Schumacher, and Stieger, *Z. physik. Chem.*, **B15**, 127 (1932).
- (3) Schumacher and Townend, *ibid.*, **B20**, 375 (1933).
- (4) Dickinson and Jeffreys, *J. Am. Chem. Soc.*, **52**, 4288 (1930).
- (5) Bowen and Cheung, *J. Chem. Soc.*, 1200 (1932).
- (6) Nagai and Goodeve, *Trans. Faraday Soc.*, **27**, 500 (1931).
- (7) Spinks and Porter, *J. Am. Chem. Soc.*, **56**, 264 (1934).
- (8) Spinks and Taube, *ibid.*, **59**, 1155 (1937).
- (9) Leighton and Mortensen, *ibid.*, **58**, 448 (1936).

TABLE 23 (Continued)
QUANTUM YIELDS OF SOME REACTIONS IN GASEOUS
AND CONDENSED SYSTEMS

Reaction	Wave Length Å	QUANTUM YIELDS				Reference
		Gas	Liquid	Water	Hexane	
$2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$	~ 2100	0.14 to 0.32	0	0	Little NH_3 de- compo- sition. Sensi- tized de- compo- sition of hexane.	§ 7.7 Table 19 (13), (14)
$\text{H}_2\text{S} \rightarrow \text{H}_2 + \text{S}$	2530	Gas	Hexane	Water (0.115 <i>M</i>)		§ 7.62 (15), (16)
	2200		0.95	0.23		
	2080	1.02		0.32		
	2070		0.97	0.43		
$\text{C}_2\text{Cl}_4 + \text{Cl}_2 \rightarrow \text{C}_2\text{Cl}_6$	4358	Chains dependent on (Cl_2) and I_{abs} , but about same in gas and CCl_4 .				(17), (18)
C_2Cl_4 oxidation (sensitized by Cl_2)	4358	Gas	CCl_4			(19)
		~ 375 at 0.01 atm.	~ 1 at 0.04 <i>M</i>			
CHCl_3 oxidation (sensitized by Cl_2)	4358	~ 100 at ~ 0.1 atm.	~ 0.6 at 0.05 <i>M</i>			(20)
$\text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2$	< 2300	Gas	Water			§ 8.8 (21), (13)
		~ 1	0.45			

- (10) Eyber, *Z. physik. Chem.*, **A144**, 1 (1929).
 (11) Warburg and Negelein, *Biochem. Z.*, **204**, 497 (1929).
 (12) Thompson and Garratt, *J. Chem. Soc.*, 524 (1934).
 (13) L. Farkas, *Z. physik. Chem.*, **B23**, 89 (1933).
 (14) Ogg, Leighton, and Bergstrom, *J. Am. Chem. Soc.*, **55**, 1754 (1933).
 (15) Forbes, Cline, and Bradshaw, *ibid.*, **60**, 1431 (1938).
 (16) Warburg and Rump, *Z. Physik*, **58**, 291 (1929).
 (17) Dickinson and Carrico, *J. Am. Chem. Soc.*, **56**, 1473 (1934).
 (18) Leermakers and Dickinson, *ibid.*, **54**, 4648 (1932).
 (19) Dickinson and Leermakers, *ibid.*, **54**, 3852 (1932).
 (20) Chapman, *ibid.*, **56**, 818 (1934); **57**, 416 (1935).
 (21) L. Farkas and Wansbrough-Jones, *Z. physik. Chem.*, **B18**, 124 (1932).
 (22) Spinks and Taube, *Can. J. Research*, **B15**, 449 (1937).

whereas the back reaction between an alkyl radical and iodine occurs readily. However, as has already been pointed out (§ 14.1), in the liquid state the conditions of a three-body collision are always present. Thus, once an ethyl radical gets past the sheath of molecules within which it was formed, the probability that it will combine with another C_2H_5 is very high. In contradiction to this simple explanation, it should be stated that Emschwiller¹² analyzed the products and found C_2H_4 and C_2H_6 but neither C_4H_{10} nor H_2 . Evidently the disproportionation reaction rather than the combination appears to be favored in the liquid state, although the reason for this is not apparent.

A summary of quantum yield measurements of various alkyl iodides in benzene and hexane solution is given in Table 24. Gibson and Iredale¹³ point out that there is an increase in the quantum yield with length of the carbon chain, further replacement of hydrogen by halogen, and change of the central carbon atom from primary to tertiary. The increase in γ with decrease in wave length is perhaps to be attributed to the increased energy given to the primary reaction products at lower wave lengths, thus promoting their chances of getting past the sheath of surrounding molecules without "primary recombination."¹⁴

It may be noted in Table 24 that, while the quantum yield of the ethyl iodide photolysis in the continuum (i.e., at 3130 to 2537 Å) is much increased in the liquid state, it is only 0.24 in the banded region at 2026 Å. This latter figure is to be compared with the value of 0.1 reported for the vapor at 90 mm. pressure in the region 2026 to 1926 Å. An explanation for this effect has already been discussed in § 8.2.

Another interesting result has been obtained by West and Paul,¹⁴ who reported that the quantum yield in C_6H_6 solution is practically the same as in hexane. Since benzene absorbs in the same region of the spectrum (cf. § 8.14) as do these

¹² Emschwiller, *Compt. rend.*, **192**, 799 (1931).

¹³ Gibson and Iredale, *Trans. Faraday Soc.*, **32**, 571 (1936).

¹⁴ Cf. West and Paul, *ibid.*, **28**, 688 (1932).

compounds, a lower result would have been expected. West and Paul attributed the result to the absorption of

TABLE 24
QUANTUM YIELDS OF THE PHOTOLYSIS OF SOME ALKYL
IODIDES, ETC., IN THE LIQUID STATE AND IN SOLUTION

Compound	γ (approx.)	λ , Å (approx.)	Solvent	Reference
Methyl iodide.....	0.052	2610	Hexane	(1)
	.0081	3130	Hexane	
Ethyl iodide.....	.24	2026	Pure	(2)
	.315	3130	Pure	(3)
	.38	2654	Pure	(3)
	.41	2537	Pure	(3)
	.58	2610	Hexane	(1)
	.30	3130	Hexane	(1)
Vinyl iodide.....	.46	2610	Hexane	(1)
	.15	3130	Hexane	(1)
Propyl iodide.....	.68	2610	Hexane	(1)
	.33	3130	Hexane	(1)
<i>i</i> -Propyl iodide.....	1.15	2610	Hexane	(1)
	.65	3130		(1)
Allyl iodide.....	.07	2610	Hexane	(1)
Iodoform.....	1.0	3650	Benzene	(4)
	1.0	3130	Benzene	(4)

REFERENCES

- (1) West and Paul, *Trans. Faraday Soc.*, **28**, 688 (1932).
- (2) West and Ginsberg, *J. Am. Chem. Soc.*, **56**, 2626 (1934).
- (3) Norton, *ibid.*, **56**, 2294 (1934).
- (4) Gibson and Iredale, *Trans. Faraday Soc.*, **32**, 571 (1936).

radiant energy by the benzene molecules and subsequent transfer to the alkyl halide molecules, i.e., to photosensitization (cf. Chapter X).

14.16 Other examples of increased quantum yield in the liquid state. In the discussion of the Franck-Rabinowitch hypothesis (§ 14.11), mention was made of the suggestion of Rollefson and Libby³ that it was actually possible for the product radicals in a primary decomposition, because of their high kinetic energy content, to force their way through

the surrounding sheath of molecules, particularly when both product radicals and surrounding molecules are small. An illustration of this phenomenon was seen in the case of the photolysis of the alkyl halides (§ 14.15). By an extension of that idea, it was possible to account for the increased quantum yield in liquid and solution and also to explain the increase in quantum yield with decrease in wave length (Table 24). In Table 25 there are two other illustrations of the same phenomenon. The effect of decrease in wave

TABLE 25

QUANTUM YIELDS OF TWO REACTIONS FAVORED IN THE CONDENSED STATE AND BY DECREASING WAVE LENGTH

(Cf. §§ 14.11, 14.15, 14.16.)

Reaction	Wave Length Å	QUANTUM YIELDS				Reference
		Gas		CCl ₄		
Ni(CO) ₄ → Ni + 4CO	4360–4060			0		(1)
	3666	0		2.2		
	3135–3010	0		2.8		
N ₂ CH ₂ COOC ₂ H ₅ (Photolysis yielding N ₂)		Heptane	C ₂ H ₅ OH	CH ₃ OH	Water	(2)
	4200	0.20	0.12	0.12		
	3650	0.31	0.15	0.14	0.12	
	3130	0.54	0.34	0.37	0.63	
	2804	1.02	1.1	1.1		
	2600	1.11	1.35	1.42	2.8	

REFERENCES

- (1) Garratt and Thompson, *J. Chem. Soc.*, 1817 (1934).
- (2) Wolf, *Z. physik. Chem.*, **B17**, 46 (1932).

length may also be seen in some of the cases cited in Table 23. In the case of ethyl diazoacetate (Table 25), it is interesting to note that the maximal effect of decreased wave length is obtained in the solvent of lowest molecular weight.

14.2 Specific solvent effects. It is possible that the primary product particle may interact with a neighboring

molecule in a variety of ways: it may displace a radical or atom of the same or different types, or it may even add on. Thus, if we imagine a compound RCl dissolved in a hydrocarbon solvent, it would be futile to attempt to estimate the quantum yield of the primary decomposition by the amount of Cl_2 liberated, because it would be only reasonable to expect that a great many of the chlorine atoms would withdraw hydrogen from the hydrocarbon or, if the hydrocarbon were unsaturated, addition might occur.

Still further, we must always bear in mind that the solvent itself may absorb light (cf. § 14.14) and that it may be photochemically responsive in the range studied. If no correction (or insufficient correction) were made for the light absorbed by the solvent, the quantum yield of the photolysis studied would appear low; if the correction made were too high, the apparent quantum yield would be high. If, as a result of such absorption, the solvent itself were affected, there is the further possibility of interaction of its products with the compound being studied, or with the products of the photolysis of that compound. In any case, it appears that, as soon as we deal with a solution, the possibilities of complication which might yield confusing results are much greater than they are when we are concerned with a pure substance.¹⁵

So far we have assumed that the molecule being studied in solution is the same molecule with which we are concerned in a study of the pure substance. Obviously the circumstances under which such a condition exists are rather limited; the molecules of a non-polar substance are usually not affected by solution in a non-polar solvent.¹⁶ However, it is seldom that such cases are studied. The more frequently investigated cases involve either association of the reactant with the solvent with formation of complex molecules, or ionization of the reactant. When the latter occurs, the ions themselves

¹⁵ An excellent illustration of the type of complication which may set in is afforded by the work of Morgan, Lammert, and Crist, *J. Am. Chem. Soc.*, **46**, 1170 (1924), on the photochemistry of alkali halides in acetophenone solutions.

¹⁶ There are exceptions to such a statement, of course. Iodine dissolved in liquid bromine (neither of which is polar) reacts with it to form iodine bromide.

may be intimately associated with a sheath of solvent molecules. The photolytic process may then involve such an ion "constellation" and be not at all related to the behavior of the pure substance from which the ion originated.

Thus it is seen that, in liquid solutions, it must be constantly borne in mind that different results may be expected depending on whether or not the substance studied is ionized, whether it or its ions form complexes with the solvent, and whether the solvent is affected either primarily by the absorbed light or secondarily by the products of the reaction.¹⁷ It is therefore important that, in studies of such solutions, the investigator identify as clearly as possible the subject of his investigation and then try, as closely as possible, to measure the object of his interest; e.g., if concerned with the photolysis of a molecule, it is well that he measure not only that molecule and the light absorbed by it but also the products of the photolysis, as well as products which might be formed by side reactions of the molecule.

In the following paragraphs we shall consider some polar substances both in polar and non-polar solvents. It will be seen that, when water is the solvent, ions will be formed in many cases. Where the ions predominate, they will be our primary concern. In the case of other substances, where ionization is but slight, the molecule may be the object of our interest. Because of the limitations of space, only a few of the more typical solutions will be discussed in this part.

14.21 Halides in solution. Nearly all of the halides (including the acids) are strong electrolytes. This means that, in aqueous solution, they are completely dissociated and that, consequently, what is being investigated is really the photochemistry of the ions. We have seen in the case of the solid salt that the alkali ion had very little effect on the position of the absorption maximum. In solutions the absorption spectra are determined exclusively by the halogen

¹⁷ In § 14.14, it has been shown that an excited benzene molecule may transmit its energy to a non-absorbing alkyl halide molecule, decomposing the latter without itself being permanently affected (i.e., by a process of photosensitization).

ions. The absorption curves are completely continuous, as shown in Figs. 51 to 53. As in the solids, the distances be-

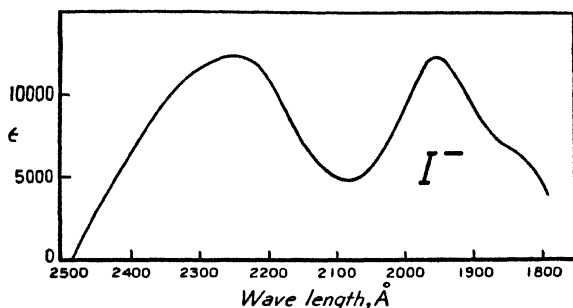


Fig. 51. Absorption Curve for the I^- Ion in Aqueous Solution, according to Scheibe, *Z. physik. Chem.*, **B5**, 355 (1929), and Franck and Scheibe, *ibid.*, **139**, 22 (1928).

tween absorption maxima are about 8000 cm^{-1} for the iodides, about 3000 cm^{-1} for the bromides, and not determinable for the chlorides.¹⁸ The explanation of the two

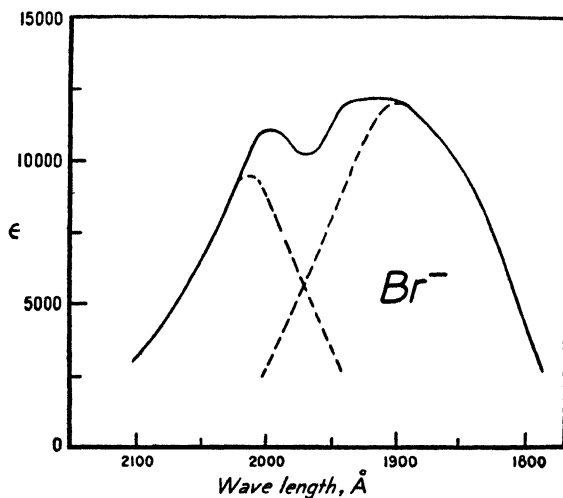


Fig. 52. Absorption Curve for the Br^- Ion in Aqueous Solution, according to Scheibe, *Z. physik. Chem.*, **B5**, 355 (1929).

¹⁸ (a) Hantzsch, *Ber.*, **59**, 1096 (1926). (b) Scheibe, *Z. Elektrochem.*, **34**, 497 (1928); *Z. physik. Chem.*, **B5**, 355 (1929). (c) Franck and Scheibe, *ibid.*, **139** (Haber-Band), 22 (1928). (d) Fromherz and Menschick, *ibid.*, **B7**, 439 (1930).

absorption maxima in the case of iodides and bromides is the same as for the solid halides (cf. § 6.22). These absorption spectra are not affected by the alkali ion, except slightly at extremely high concentration.

In the solid alkali halides we were concerned with the photochemistry of the halogen ion in the crystal field. In

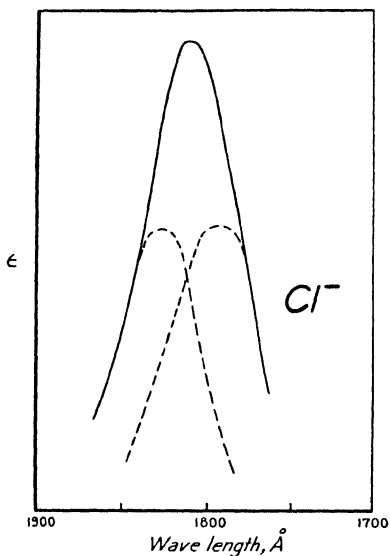
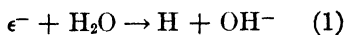


Fig. 53. Absorption Curve for the Cl^- Ion in Aqueous Solution, according to Scheibe, *Z. physik. Chem.*, **B5**, 355 (1929). $\epsilon_{\text{max}} \approx 10,000$.

aqueous solution, the primary steps involved relate only to the negative ion and the neighboring water molecules. In the solid halides, the primary process involved is the removal of an electron from the halogen ion. In solution, the potential barrier to be overcome, according to Franck and Scheibe, is the electron affinity of the anion as modified by its hydration.^{18c} A model is suggested in which the electron moves from the halogen ion to a water molecule



thus yielding a hydrogen atom and a hydroxyl radical.

¹⁹ In acids the latter may then combine with a free hydrogen ion to yield water, and the overall "primary" process may then be said to produce a halogen atom and a hydrogen atom which would tend to recombine, thus reducing the quantum yield.

14.22 Hydriodic acid. Warburg and Rump²⁰ studied the case of hydrogen iodide both in aqueous solution and in hexane. Their results in water, as shown in Table 26,

¹⁹ Franck and Haber, *Sitzb. kgl. preuss. Akad. Wiss.* 250 (1931); Haber, *Naturwissenschaften*, **19**, 450 (1931).

²⁰ Warburg and Rump, *Z. Physik*, **47**, 305 (1928).

indicate in a rough way that the quantum yield falls off both at low HI concentrations and at higher wave lengths. Unfortunately it is impossible to judge how reliable the figures are.²¹ If correct, their apparent discordancies are quite challenging. Warburg and Rump reported that, with initial HI concentrations as low as 0.01 *N*, no yield was detected (i.e., $\gamma = 0$) at 2220 Å. The data presented certainly justify verification and extension of the investigation over a greater range of wave length.

TABLE 26
QUANTUM YIELD OF PHOTOLYSIS OF HYDROGEN IODIDE
IN WATER

λ N HI	2070 Å	2220 Å	2820 Å
0.8	.336	.078	.114
3.75	.959	.455	.457
7.5	2.21	1.21	.538

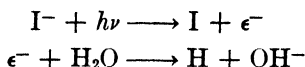
The results of the studies in hexane solution²⁰ are also anomalous. In this case the quantum yields increase with increasing wave lengths and with increasing concentration, approaching ~ 2.0 as a limit at 2820 Å in 1.16 *N* solution. Inasmuch as the hydrogen iodide in hexane solution exists in the form of molecules, a close analogy to the gaseous reaction would have been expected. It is certain that the results reported are to a great extent affected by the calculations, since in this case allowance had to be made for the absorption by hexane itself (which must have been contaminated, to account for absorption in that region), as well as for the absorption by iodine. However, since the investigators report only the results of their calculations, it is impossible to determine whether this is so. The most reasonable conclusion to draw is that the photolysis of hydrogen iodide in hexane is similar to that in the gaseous state so long as the

²¹ Difficulties were introduced, into the calculations of results, by such factors as light absorption by I_3^- , which seemed to be present even in the original solution.

experiments are conducted in a region where the solvent itself is not particularly sensitive.

Until such a time as the quantum yields, both in aqueous solution and in hexane, are more definitely established, it seems futile to concern ourselves too much with theories offered to explain the precise results reported.

14.23 Alkali halide solutions. Little remains to be said (after § 14.22) about the photochemical behavior of halide solutions. The reactions of the alkali halides are those of the halogen ions as modified by the presence of the alkali metal ions. According to Butkow,²² when solutions of iodides (free of air) are illuminated at $\lambda < 2700 \text{ \AA}$, iodine is liberated and the solutions become alkaline. The photochemically sensitive range coincides with the absorption spectrum of the iodide ion. The explanation is the following set of reactions:



The iodine atoms combine to form molecules, as do the hydrogen atoms. The formation of the hydroxyl ion accounts for the alkaline reaction. When bromides are studied, the quantum yields are very low (even for iodides, there is no approach to a quantum yield of unity); for chlorides, there is no liberation of chlorine. The explanations for these results so far offered are not particularly satisfactory. It seems that further investigation of this subject would be justified.

14.3 Other ions in solution. Besides the halides, only a few electrolytes have been studied photochemically. Of these, very few are principally ionic in solution. Although they display absorption spectra (characteristic of the ions), they do not necessarily give any products (*v.* the chlorides, § 14.23), and the absorption regions may be at a wave length not ordinarily convenient or accessible for study. Aqueous solutions cannot be investigated below the quartz region on account of the absorption by water itself.

²² Butkow, *Z. Physik*, **62**, 71 (1930).

14.31 Hydroxides in solution. Ley and Arends²³ have investigated the absorption spectrum of hydroxide ions in solution and have obtained results which are summarized in Fig. 54 for the typical case of sodium hydroxide. As in the case of the halide ions, the absorption maximum presumably corresponds to the electron affinity of the hydroxide ions as modified by the solvent. Although a photochemical yield might be expected on illumination of hydroxide solutions at $\sim 1900 \text{ \AA}$, no such result has been observed.

14.32 Sulfur compounds. According to Ley and Arends,²⁴ the sulfates begin to absorb below $2000 \text{ \AA}$, while the bisulfates are even more transparent. The bisulfites do not absorb above $2250 \text{ \AA}$.²⁵ None of these have been studied photochemically because of the obvious difficulties.

Potassium persulfate solutions have been photochemically studied by several investigators.²⁶ Crist²⁷ found the quantum yield of the overall reaction

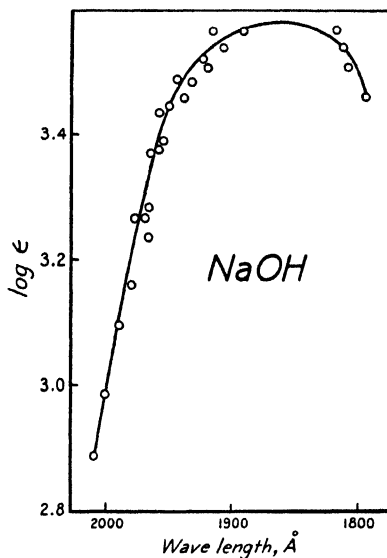
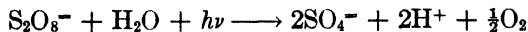


Fig. 54. Extinction Coefficient of Sodium Hydroxide in Aqueous Solution, according to Ley and Arends, *Z. physik. Chem.*, **B6**, 240 (1929).

$$\epsilon = \frac{1}{cl} \log \frac{I_0}{I}$$

²³ Ley and Arends, *Z. physik. Chem.*, **B6**, 240 (1929). For the electron affinity of OH^- , see Goubeau and Klemm, *ibid.*, **B36**, 362 (1937), who give a lower value of 48 kcal.

²⁴ Ley and Arends, *Z. physik. Chem.*, **B15**, 311 (1931).

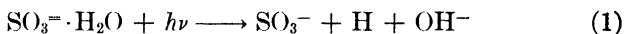
²⁵ Albu and Goldfinger, *Z. physik. Chem.*, **B16**, 338 (1932).

²⁶ Dhar, *Proc. Akad. Vetensk.*, **23**, 308 (1920); Elbs and Neher, *Chem.-Z.*, **45**, 1113 (1921); Morgan and Crist, *J. Am. Chem. Soc.*, **49**, 16, 338, 960 (1927).

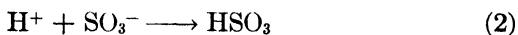
²⁷ Crist, *J. Am. Chem. Soc.*, **54**, 3939 (1932).

to be ~ 1.0 in neutral and alkaline solutions at wave lengths from 3020 Å to 2540 Å. He was unable to suggest a completely satisfactory mechanism.

Sulfite solutions have been rather thoroughly investigated. The continuous absorption region begins at ~ 2655 Å; the extinction coefficient continues to increase toward longer wave lengths.²⁵ Franck and Haber¹⁹ ascribed the continuous absorption to the electron affinity spectrum of SO_3^- as modified by the solvent, and attributed the absorption to the primary process²⁸



This reaction and the reactions subsequent to it have been studied by Haber and Wansbrough-Jones,²⁹ who found that the quantum yield of decomposition of sulfite ion in oxygen-free solution is only ~ 0.07 at $\text{pH} = 9.6$ and decreases with increasing alkalinity. Among the products, there are mainly H_2 and $\text{SO}_4^{=}$ ion; also, several parts per thousand of sulfite ion originally affected recombine as dithionate ion; i.e., $2\text{SO}_3^- \rightarrow \text{S}_2\text{O}_6^{=}$. The main steps which they proposed (to explain their results) are:



and either



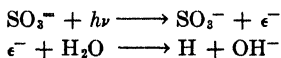
which is the reverse reaction, or



The last reaction accounts for the main reaction products.

It is well known that, when aqueous sulfide solutions are illuminated in the ultraviolet, sulfur is eliminated. However, no quantitative measurements have been performed. The absorption spectra of HS^- and $\text{S}^{=}$ ions were investigated by

²⁸ An equivalent model appears more desirable:



²⁹ Haber and Wansbrough-Jones, *Z. physik. Chem.*, **B18**, 103 (1932).

Ley and Arends;²⁴ the continua begin at $\sim 2900 \text{ \AA}$ for both, whereas for hydrogen sulfide (which is practically undissociated) the continuum begins at $\sim 2600 \text{ \AA}$. Data on the photolysis of H_2S in water and hexane is included in Table 23.

14.33 Nitrates. Although there have been many photochemical investigations of nitrates in solution,³⁰ there is a surprising dearth of quantitative information. The absorption spectrum of the nitrate ion is shown in Fig. 55. As the concentration of nitric acid in solution is increased, there is a continuous variation in the shape of its absorption curve (v. Fig. 56, p. 376). Doubtlessly, at high concentrations it is not the simple ionic form which is responsible for the shape of the extinction curve; a similar curve is obtained in ether solutions. As yet the photochemistry of the nitrates has not been fully elucidated.

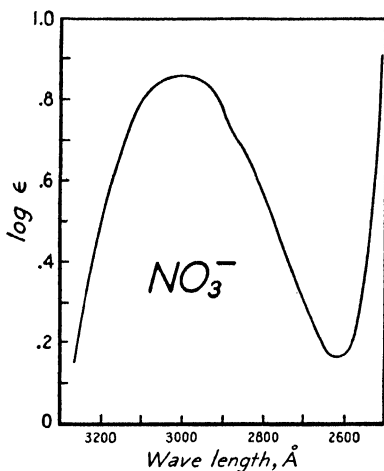


Fig. 55. Extinction Coefficient of the Nitrate Ion in Aqueous Solution, according to Ley and Volbert, *Z. physik. Chem.*, **130**, 308 (1927).

$$\epsilon = \frac{1}{cl} \log \frac{I_0}{I}$$

On illumination of nitrate solutions in the ultra-violet, O_2 is evolved in all cases.³¹ Up to 50 per cent of the total initial concentration of nitrates may be decomposed in this way. Nitrites are thus produced and, with sufficiently intense illumination, ammonia is formed.

³⁰ Scheibe, *Ber.*, **59**, 2616 (1926). Baly, Morten, and Riding, *Proc. Roy. Soc. (London)*, **113**, 709 (1927). Von Halban and Eisenbrand, *Z. wiss. Phot.*, **25**, 149 (1928). Ley and Volbert, *ibid.*, **23**, 41 (1925); *Z. physik. Chem.*, **130**, 308 (1927). Shljivcić and Nikolić, *Bull. soc. chim. roy. Yougoslav.*, **6**, 159 (1936); **7**, 43 (1936). Mudrovčić, *ibid.*, **7**, 41 (1936). Cultrera, *Gazz. chim. ital.*, **66**, 440 (1936). Vogels, *Bull. sci. acad. roy. Belg.*, **22**, 320 (1936).

³¹ Warburg, *Ber. Berliner. Akad.*, 1228 (1918); Cultrera, ref. 30. Cf. § 6.5, for the behavior of solid nitrates.

14.34 Bichromates and permanganates. The visible absorption spectra of these substances are without particular photochemical interest. They are attributable, not to electron affinity spectra, but merely to electronic transitions within the ion; e.g., an electron jump into the third, incompletely filled, shell of the metallic atom. The pronounced band structure of the permanganate ion³² is in correspondence with the conclusion that all that occurs in this case is an excitation of the negative ion. The failure to obtain decomposition in the visible conforms with this hypothesis.

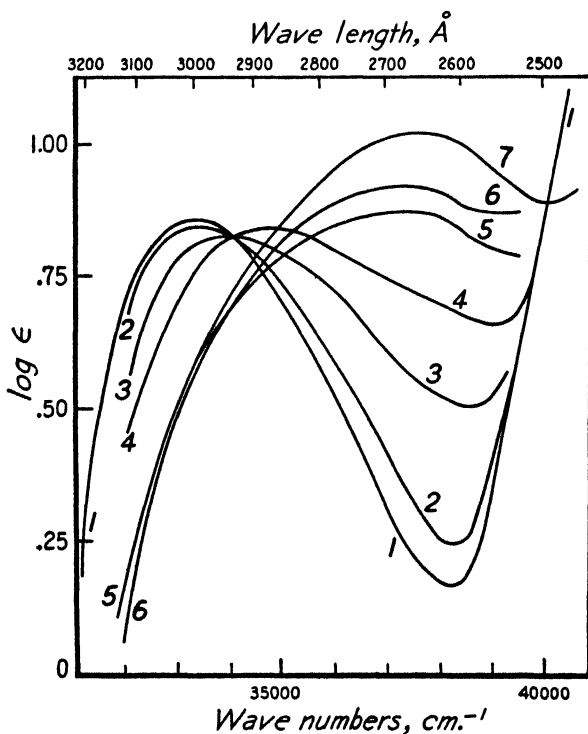


Fig. 56. Extinction Coefficient of Nitric Acid at Various Dilutions in Water and in Ether, according to Halban and Eisenbrand, *Z. physik. Chem.*, **132**, 433 (1928). Dilutions in water: (1) very dilute, (2) 1.94 *N*, (3) 6.86 *N*, (4) 9.22 *N*, (5) 14.8 *N*, (6) 15.2 *N*; dilution in ether: (7) 0.053 *N*.

³² Schnetzler, *Z. physik. Chem.*, **B14**, 214 (1931). For a summary of the literature, see Lange and Schusterius, *ibid.*, **159**, 295 (1932).

Both chromates and permanganates absorb in the ultra-violet. Although the spectrum of permanganate is again band-like in this region, photochemical decomposition is observed in both cases.³³ It is likely that the initial step is the separation of an oxygen atom; however, there is no definite information on this point. Technological use is made of the oxidation reactions of the bichromates on various proteins or gums, for example, in the photo-offset process and in processes of photo-engraving. However, the bichromates are not necessarily the photoactive components in all photochemical oxidations in which they take part. For example, quinine is the photoactive component in its photo-oxidation by bichromate.³⁴

14.35 Cations in solution. This title is really introduced formally. We have no evidence in any specific case that a decomposition (such as that postulated in the model for aqueous halides) is ever involved in the photochemistry of metal ions. The absorption spectra of such metal ions as Cr^{+++} are attributed to an electron jump of an electron to an unfilled shell.³⁵ However, there is no evidence of any photochemical reaction of chromic ion. Neiger and Neuschul³⁶ have studied the photochemical reduction of ferric gluconate in aqueous solution, while Prasad and his co-workers³⁷ have studied the photoreduction of ferric chloride in various alcoholic solvents. It is interesting to note that in neither case is a photoreaction of the cation necessarily concerned. In the case of the gluconate, it may be the anion which is photoactivated. In both cases we are dealing with weak electrolytes; it is quite possible that a photoreaction of the molecule as a whole may be the actual mechanism. Prasad and Mohile have suggested an alternative mechanism in which the Fe^{+++} ion is activated and then reacts with a

³³ Cf. Rao, *Proc. Indian Acad. Sci.*, **6A**, 293 (1937).

³⁴ Forbes, Heidt, and Boissanas, *J. Am. Chem. Soc.*, **54**, 960 (1932); Forbes, *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 1 (1935).

³⁵ Deutschbein, *Z. Physik*, **77**, 496 (1932).

³⁶ Neiger and Neuschul, *Z. physik. Chem.*, **A177**, 355 (1936).

³⁷ Prasad and Mohile, *Proc. Nat. Acad. Sci. India*, **6**, 261 (1936); Prasad, Mohile, and Nigudkar, *J. Univ. Bombay*, **5**, Part 2, 142 (1936).

solvent molecule. In any event the model is altogether different from a photolysis model as set up for the halogen ions.

14.4 Photosensitization in solution. Instances of this phenomenon have already been cited. The quantum yield of the photolysis of the alkyl halides is practically the same in hexane and benzene solution, although the benzene is known to absorb in the photoactive region (§ 14.15). The explanation proposed by West and Paul¹⁵ is simply that the energy absorbed by the benzene molecule is transferred to the alkyl halide molecule, which thereupon behaves as if it had absorbed the radiation. A second case is the photolysis of NH_3 in hexane solution (Tables 20 and 23). Practically none of the NH_3 is decomposed, but the hexane, which is itself inert to the absorbed radiation, is decomposed.³⁸ Of course, it is not possible to state whether the first step is the decomposition of NH_3 into NH_2 and H , or the activation of NH_3 . That the first reaction actually does take place seems to be indicated by a slight decomposition of the ammonia. However, there is also the possibility that the energy is transferred from the activated NH_3 molecule to an adjoining hexane molecule (see §§ 14.1 and 14.11), and that the latter decomposes as a result of the process.

It has been customary to speak of the uranyl oxalate decomposition as if it also were an example of photosensitization. However, it now seems to be established that, in this case, the existence of an active complex is involved (see § 14.7).

Glycolic and glyoxylic acids are photo-oxidized in aqueous solution by ordinary lamp light in the presence of chlorophyll, UO_2^{++} , ferric salts, or dyestuffs of the eosin class as sensitizers.³⁹

Methyl alcohol is decomposed to H_2 and HCHO at 2000 to 1850 Å. Fricke and Hart⁴⁰ have stated that water may act as the photosensitizer, but the evidence is not sufficient to warrant such a conclusion.

³⁸ L. Farkas, *Z. physik. Chem.*, **B23**, 89 (1933).

³⁹ Baur, *Helv. Chim. Acta*, **19**, 234 (1936).

⁴⁰ Fricke and Hart, *J. Chem. Phys.*, **4**, 418 (1936); cf. § 8.5.

14.5 A case of inhibition: decomposition of hydrogen peroxide. Hydrogen-peroxide solutions are stabilized by some substances of an acid character, as well as by such well-known preservatives as acetanilide; on the other hand, free base markedly accelerates the thermal decomposition.⁴¹ The photochemical decomposition is retarded about twenty-five times more efficiently by alkalis than by acids, while a great host of substances neither strongly acid nor basic (including acetanilide)⁴² have marked inhibitory properties.⁴³

Various factors may be responsible for the retardation of the photolysis: (a) removal of the OH radicals primarily formed, thus decreasing the number of chains started;⁴⁴ (b) absorption of effective radiation; (c) interruption of chains.⁴⁵

As for process (b), it cannot be effective generally for the very obvious reason that some of the inhibitors used (e.g., ethyl alcohol and the alkalis) do not absorb in the photo-active range. The mechanism of process (c) is as yet imperfectly elucidated. Jeu and Alyea⁴⁵ made an interesting comparison of the effectiveness of various inhibitors in reactions of different types: (1) the photopolymerization of vinyl acetate (cf. Table 22); (2) the auto-oxidation of sodium sulfite; (3) the photolysis of hydrogen peroxide. They found that the first two are retarded in the same order of effectiveness by different reactants, and that there is no simple relation between the orders of activity of the different retardants in the case of H_2O_2 and in the other cases. Thus it must be concluded that, if the photolysis of H_2O_2 in solution is a chain process,⁴⁶ the chain-breaking mechanism must be different from that in the other reactions studied.

⁴¹ Cf. Bailey, *The Retardation of Chemical Reactions*, Longmans, Green & Co., New York, 1937, p. 274.

⁴² Mathews and Curtis, *J. Phys. Chem.*, **18**, 166, 521 (1914).

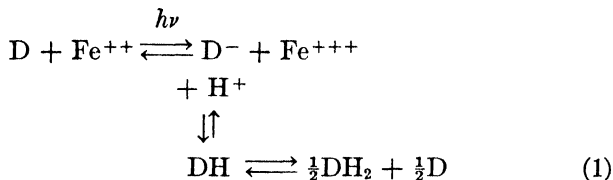
⁴³ Anderson and Taylor, *J. Am. Chem. Soc.*, **45**, 650, 1210 (1923).

⁴⁴ Dam and Shvartz, *Acta Physicochim.*, U.R.S.S., **3**, 291 (1935).

⁴⁵ Cf. Jeu and Alyea, *J. Am. Chem. Soc.*, **55**, 575 (1933); Richter, *J. Chem. Soc.*, 1219 (1934).

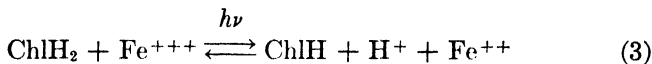
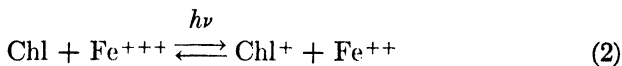
⁴⁶ The quantum yield varies with the experimental conditions between 1 and 500. Cf. Henri and Wurmser, *Compt. rend.*, **156**, 1012 (1913); Kornfeld, *Z. wiss. Phot.*, **21**, 66 (1921); Allmand and Style, *J. Chem. Soc.*, 596, 606 (1930); Heidt, *J. Am. Chem. Soc.*, **54**, 2840 (1932); Richter, *J. Chem. Soc.*, 1219 (1934).

14.6 Oxidation and reduction. As an outgrowth of studies involving the reactions of free atoms in the gaseous state and in solution, Rabinowitch and his co-workers⁴⁷ investigated the photochemical reactions of various dyes in solution. The thionene dyes, when illuminated in a solution containing ferrous ions, act as oxidizing agents. At low light intensities a conveniently studied steady state is reached; this may be represented schematically by the reactions



where D represents a molecule of the dye and DH_2 is obviously the leuco-base. The reaction is reversible in the dark, and the position of the steady state is evidently determined by the intensity of the light.

Chlorophyll, on the other hand, behaves in precisely the opposite fashion. Its illuminated solutions have reducing properties, and its reaction with ferric ion may be represented by one of the equations:



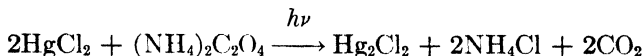
where Chl and ChlH_2 represent the chlorophyll molecule in reactions (2) and (3) respectively. Rabinowitch studied the steady state conditions with Fe^{+++} , Ce^{++++} , I^- , and Cu^{++} , and came to the conclusion that the reaction between the excited chlorophyll molecule and the other reactant molecule always went on the first collision. Interestingly enough, he found that, although chlorophyll excited in this way served

⁴⁷ Cf. Rabinowitch and Weiss, *Nature*, **136**, 1098 (1936); Porret and Rabinowitch, *ibid.*, **140**, 321 (1937); Weiss, *ibid.*, **141**, 248 (1938); Rabinowitch and Weiss, *Proc. Roy. Soc. (London)*, **A162**, 251 (1937).

as a reducing agent for formic acid, it had no such effect on carbon dioxide. Its activity in the process of photosynthesis is perhaps to be attributed in that case to the fact that the conditions are considerably different. It is present, not as a solute, but as an adsorbed layer on the surface of a colloidally dispersed system. (See also § 15.43.)

14.7 Some photochemical reactions involving oxalates.

A number of reactions have been studied in which oxalates are either decomposed or oxidized to carbon dioxide. One of these is the so-called *Eder reaction*, in which solutions of ammonium oxalate and mercuric chloride are mixed; the net reaction is expressed by the equation



If the reaction mixture is made up from ordinary materials, it is sensitive to visible light. However, Winther⁴⁸ showed that this sensitivity is due to traces of iron salts present in the materials commercially available. Concentrations of ferric chloride as low as 3×10^{-4} moles per liter are sufficient to cause an appreciable reaction with blue light.

The reaction is further complicated by an inhibiting action of oxygen and an induced dark reaction which occurs if both oxygen and ferric chloride are present.⁴⁹ The reaction proceeds even with carefully purified reactants at $\lambda \sim 3000$ Å. Apparently the mechanism of the reaction involves long chains; but no measurements of quantum yield have been made, except the observation of Roseveare that chains of the order of 6×10^5 steps are initiated by x-rays. The reaction is primarily of historical interest.

The uranyl-sensitized decomposition of oxalic acid is of particular importance because of the careful study of Leighton and Forbes⁵⁰ of the quantum yield at many wave lengths. If the concentration of the oxalate is at least

⁴⁸ Winther, *Z. wiss. Phot.*, **8**, 197, 237 (1910), and earlier papers.

⁴⁹ Roseveare, *J. Am. Chem. Soc.*, **52**, 2612 (1930).

⁵⁰ W. G. Leighton and Forbes, *J. Am. Chem. Soc.*, **52**, 3139 (1930). Cf. Forbes et al., *ibid.*, **53**, 3973 (1931); **55**, 4459 (1933); **56**, 2363 (1934); **57**, 1935 (1935).

five times that of the uranium, the net reaction is merely the decomposition of oxalic acid into carbon dioxide, carbon monoxide, and water. Under these conditions, the rate depends solely on the light absorbed and the quantum yield is in the range 0.5–0.6 for most wave lengths.

At low oxalate concentrations (i.e., oxalate/uranyl ratios less than 1), some reduction of the uranium to the tetravalent form occurs.⁵¹ The lower the oxalate concentration, the greater is this reduction as compared to the decomposition of the oxalate. The photoactive substance involved in the simple decomposition appears to be a complex of uranyl and oxalate. The low quantum yield must be attributed to deactivation of this complex either by the solvent or by some change which produces no net reaction. The reduction which occurs at low oxalate concentrations may be due partially, or even entirely, to free uranyl ions.

Other reactions which have been the subject of several investigations are the reactions of iodine and bromine with oxalate, in which the halogen is reduced to the halide ion and the oxalate oxidized to carbon dioxide. These reactions proceed both thermally and photochemically; however, the latter can be made the predominant reaction at low temperatures. Berthoud and Bellenot⁵² have shown that the rates of the photo-oxidation of neutral oxalates by bromine and iodine are proportional to the square root of the absorbed energy. These results have been confirmed by others.⁵³ Griffith, McKeown, and Winn extended the work with bromine to include acid solutions.⁵⁴ They found two distinct reactions: one involving HC_2O_4^- , and the other $\text{C}_2\text{O}_4^{=}$. Both reactions are retarded by bromide ion, but the retardation is different in each case.

A mechanism has been set up which accounts for the experimental facts. The effective primary step is the photo-

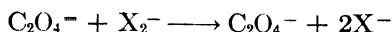
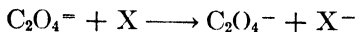
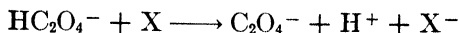
⁵¹ Pitzer, Gordon, and Wilson, *ibid.*, **58**, 67 (1936).

⁵² Berthoud and Bellenot, *J. chim. phys.*, **21**, 308 (1924); *Helv. Chim. Acta*, **7**, 307 (1924).

⁵³ Briers, Chapman, and Walters, *J. Chem. Soc.*, 562 (1926); Allmand and Young, *Trans. Faraday Soc.*, **27**, 515 (1931).

⁵⁴ Griffith, McKeown, and Winn, *Trans. Faraday Soc.*, **29**, 369, 386 (1933).

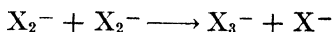
dissociation of the trihalide ion X_3^- . The bulk of the halogen atoms formed in this step are converted into X_2^- by the equilibrium $X + X^- \rightleftharpoons X_2^-$. The rate determining reactions are:



These are followed by



and the reaction



terminates the chains.

14.8 Effect of circularly polarized light. A beam of plane polarized light may be looked upon as the resultant of two beams of circularly polarized light, with the rotations in opposite direction and of equal intensity. According to this model, the rotation of the plane of polarized light by an optically active substance is caused by the difference in the indices of refraction exhibited by the two beams in that substance.⁵⁵ Conversely, it would be expected that a circularly polarized beam of light would exhibit different indices of refraction in two optically active isomers. This effect has been studied and discussed principally by W. Kuhn and his co-workers.⁵⁶

Accompanying this difference in the indices of refraction there may be a slight difference in the absorption coefficients.⁵⁷ Difference in absorption coefficients implies a difference in the transition probabilities of the states concerned. If part of the absorbed energy reappears as fluorescence, we should expect a difference in the yield of fluorescent light in the region of differing absorption (cf. § 3.22). If

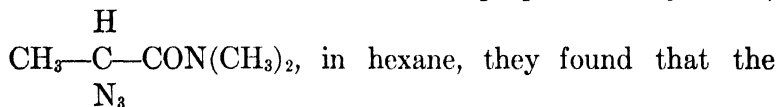
⁵⁵ Cf. R. W. Wood, *Physical Optics*, Macmillan Company, New York, (3rd Ed.) 1934, p. 572 et seq.

⁵⁶ W. Kuhn, *Naturwissenschaften*, **26**, 289, 305 (1938).

⁵⁷ There is no simple correlation between index of refraction and absorption coefficient. See ref. 56.

the absorbed light is photochemically active (in producing decomposition) and the quantum yield is less than unity, the quantum yields of products for the same beam of circularly polarized light should differ for two optically active isomers. Superimposed on such an effect is that caused by the difference in the absorption of the light beam concerned.

The possibility of separating optically active isomers photochemically by means of circularly polarized light has been discussed in detail by Kuhn and Knopf.⁵⁸ In the case of a solution of α -azidopropiondimethylamide,



quantum yield of the decomposition is unity for the two forms but that the absorption coefficients for circularly polarized light differ by 2 to 3 per cent. Illumination of the racemic mixture with right-handed circularly polarized light caused the mixture to become dextrorotatory, whereas left-handed circularly polarized light has the opposite effect. The observed rotations of plane polarized light after 40 per cent decomposition were of the order of one degree.

⁵⁸ Kuhn and Knopf, *Z. physik. Chem.*, **B7**, 292 (1930). Cf. Zocher and Coper, *ibid.*, **132**, 313 (1928).

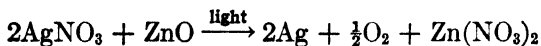
CHAPTER XV

HETEROGENEOUS REACTIONS

15.1 Importance of heterogeneous reactions. From the technological point of view this class of reactions, which we have reserved for our final chapter, appears the most significant. It includes the photochemistry of the white pigments, which are the common *bodies* in paints; photography, which is the only large photochemical industry; and photosynthesis, without which life itself might be non-existent. Consequently any emphasis on the importance of this class of photochemical reactions seems to be unnecessary. In the next few sections it will be seen, however, that these reactions present aspects which make them quite as interesting theoretically as they are technologically.

15.2 White pigments as sensitizers. The earliest mention of this class of reaction seems to be by Eibner,¹ who found that Prussian blue is reduced by light in the presence of glycerine or sugar and *zinc oxide*. Other investigations on ZnO have been conducted by Baur and his co-workers,² and by Winther.³ The latter found that dyes are decolorized on illumination in mixtures with ZnO and glycerine, and that *white lead* is darkened under similar conditions.⁴

Baur and Perret state that AgNO_3 in aqueous solution in contact with ZnO is reduced by light according to the reaction



with the possible formation of an unstable silver peroxide as an intermediate product. The disappearance of the ZnO

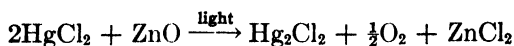
¹ Eibner, *Chem. Zeitung*, **35**, 753, 774, 786 (1911).

² (a) Baur, *Helv. Chim. Acta*, **1**, 186 (1918); (b) Baur and Perret, *J. chim. phys.*, **23**, 97 (1926); (c) Baur and Neuweiler, *Helv. Chim. Acta*, **10**, 901 (1927).

³ Winther, *Z. wiss. Phot.*, **21**, 141, 168, 175 (1921).

⁴ Goodeve, *Trans. Faraday Soc.*, **33**, 340 (1937).

in this case is regarded as a side reaction. Solutions of HgCl_2 are reduced according to



with the disappearance of the sensitizer again regarded as a secondary process. Methylene blue solution illuminated in the presence of ZnO yields both an oxidation product and a leuco-derivative.

Independent investigators ^{2,4} have shown that there is a sensitized reaction between water and oxygen in the presence of ZnO , yielding H_2O_2 . On the other hand, the claim ³ that ozone is formed on illumination of ZnO in air has been shown to be incorrect. ⁵

Both Keidel ⁶ and Wagner ⁷ have described the action of *titanium dioxide* in discoloring certain dyestuffs. According to Renz, ⁸ TiO_2 is reduced by light in the presence of glycerine. Usually dyes attacked by TiO_2 are not attacked so much by ZnO , and vice versa. ⁴ It may be noted that TiO_2 is acidic, whereas ZnO is basic.

Lithopone (a mixture of barium sulfate and zinc sulfide) is apparently not a good sensitizer but is itself decomposed by light below 3600 Å. ⁹

Barium sulfate is photochemically inactive. ¹⁰

It is, of course, striking that each one of the compounds mentioned is important as a white pigment in paints. Their properties as photosensitizers, as may be imagined, frequently decrease their utility. The *chalking* of paints made with titanium dioxide, as well as the deterioration of zinc oxide paints in sunlight, is perhaps to be attributed to photosensitization. ¹¹

Until recently all that has been known of the photosensi-

⁵ McMorris and Dickinson, *J. Am. Chem. Soc.*, **54**, 4248 (1932).

⁶ Keidel, *Farben Zeitung*, **34**, 1242 (1929).

⁷ H. Wagner, *ibid.*, **34**, 1243 (1929); Wagner and Zipfel, *ibid.*, **37**, 1480 (1932).

⁸ Renz, *Helv. Chim. Acta*, **4**, 961 (1921).

⁹ Pfund, *Proc. Am. Soc. Test. Mat.*, **23**, II, 369 (1923).

¹⁰ H. A. Gardner, *Physical and Chemical Examination of Paints*, Inst. of Paint & Varnish Research, Washington, D. C., 1935, p. 235.

¹¹ Cf. H. S. Taylor, *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 66 (1935).

tive range of these substances is that the light from a mercury arc filtered through glass is able to activate the reactions described for ZnO and TiO₂; i.e., light of $> 3300 \text{ \AA}$ is actually effective. However, Goodeve⁴ has now undertaken a systematic study of these compounds and has established that the activity is not due to decomposition of ZnO or TiO₂ in their photoactive range. The conclusion that photosensitization is definitely involved and that the pigments are the sensitizers derives from his studies on the absorption spectra of those substances.

The absorption thresholds as determined by Goodeve are given in Table 27. In order for these substances to be effective as photosensitizers, the energy absorbed must not be dissipated as heat. Consequently we can expect that these substances would prove to be fluorescent, as they actually are.^{4, 12} Furthermore, they appear capable of sensitizing fluorescence (which is ordinarily weak) in pure, raw linseed oil. It seems evident that light energy absorbed by the pigments can be transferred to other substances to raise them to excited states, and that a merely thermal process is not involved. Indeed, it also appears that light energy may be absorbed in one portion of a submicroscopic crystal and transmitted intact to produce photochemical reaction at some remote point of contact with the sensitive substance.^{4, 12a}

TABLE 27
ABSORPTION THRESHOLDS OF WHITE PIGMENTS

Pigment	Approximate Threshold $\text{\AA}$	Minimum Quantum kcal.
Titanium oxide (pure)	4000	71
Zinc oxide	3850	74
Lead carbonate	2740	104
Lithopone (Pfund)	3510	81

¹² Cf. Radley and Grant, *Fluorescence Analysis in Ultraviolet Light*, Chapman & Hall, Ltd., London, (2nd Ed.) 1935, p. 166.

^{12a} The theory involved has been discussed by Frenkel, *Physik. Z. Sowjet-union*, **9**, 158 (1936).

Goodeve and Kitchener¹³ approached the problem directly by studying the bleaching of a dye, "Chlorazol Sky Blue FF," in the presence of TiO_2 . They found that the quantum yield increases sharply at $< 4000 \text{ \AA}$ and attains a maximum at $\sim 3450 \text{ \AA}$. Bleaching extends from about $7200 \text{ \AA}$ to the far ultraviolet, although it is rather weak. The maximum occurs at a wave length where absorption by the dye has become weak but where the TiO_2 is strongly absorbing. This clearly indicates that photosensitization is involved. The existence of a maximum is attributed to the fact that TiO_2 has a very high absorption coefficient, which rapidly increases beyond $3500 \text{ \AA}$. Thus the effective bleaching by the light is limited to the surface layer.

15.3 Photography. Photographically sensitive emulsions are made by the suspension of finely divided silver chloride or bromide in a gelatin substrate. The photographically sensitive range of the emulsion depends upon the conditions of precipitation of the halide, the particle size, the composition of the gelatin, and the presence of various sensitizers. When the emulsion is exposed to light in the photoactive range, a *latent image* is produced. Such an image is invisible to the naked eye. It may be *developed* by bathing the film or plate in a suitable reducing agent, whereupon the visible image is produced. Thereafter the plate is washed to remove excess reducing agent, and is transferred to a fixing bath to remove *undeveloped* silver halide.

In the actual photographic process, theoretical questions arise concerning the factors which affect the photosensitive range, the formation and nature of the latent image, and the mechanism of development. It may be seen that, although the subject of photography is largely concerned with the photochemistry of the silver halides, there are also other factors involved.

The latent image in silver halide crystals has already been discussed (§ 6.31). Two suggestions have been made as to

¹³ Goodeve and Kitchener, *Trans. Faraday Soc.*, **34**, 570 (1938).

its nature. The first, suggested by Pohl, is based on an analogy to the F centers in the photochemistry of the alkali halides (cf. § 6.2 et seq.). According to the second, the latent image consists of microscopic or submicroscopic silver agglomerates. In § 6.31, reasons were given in favor of the idea that the latent image in actuality is made up of both F centers and agglomerates, the former acting as a reserve from which additional or larger agglomerates can be formed under certain conditions (e.g., if the halide crystals are fractured after exposure). However, this is by no means a generally accepted point of view, even by the proponents of the perforated lattice model of the photochemistry of the alkali halides.¹⁴

There are similarly contrasting points of view as to the manner in which the agglomerates are formed. Reasons have been given for the idea that they are produced by the migration of electrons to a focus of disturbance. At that point the electron may react with a silver ion, forming a free atom which serves to spread the area of disturbance. According to that point of view, the silver atom agglomerates are formed by discharge of silver ions already present in that region. The halide ions in that region may now lose their charge to the crystal, and be absorbed and fixed by the gelatin.^{14a} That a large portion of them are not so fixed is indicated by the Herschel effect. The developed density of an exposed plate can be lessened, but not brought back to the unexposed value, by exposing it to red light.¹⁵ Presumably the phenomena of formation of the latent image cannot be reversed, once the halogen atoms are fixed in the gelatin.

According to another point of view presented in a quantum mechanical way by Gurney and Mott,¹⁴ actual ions of silver migrate to a locus (e.g., a particle of silver or silver sulfide) of increased electron concentration. This hypothesis

¹⁴ Cf. Gurney and Mott, *Proc. Roy. Soc. (London)*, **A164**, 151 (1938).

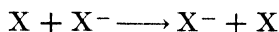
^{14a} Such an electron diffuses within the crystal to a bromine atom formed in the initial photolytic process, thus recreating an ion.

¹⁵ Hay, *Handb. wiss. Photographie*, **5**, 317 (1932).

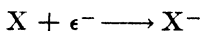
differs from the one discussed in the preceding paragraph in the suggestion of a second step. Both involve the migration of the electrons produced in the primary process. Both involve the idea that these electrons may gather around a center of disturbance. But, whereas the former suggests that the ions in the vicinity of that center agglomerate as they are discharged, the latter¹⁴ suggests that there are conditions which favor the building up of local electron atmospheres which attract the positive silver ions in the vicinity.

However, apart from the various theories proposed to explain the latent image and its method of formation, it is certain that it is the presence in the halide grain of metallic silver that renders it developable.¹⁶ This is known from the simple fact that the developer continues to act on a grain long after any special configuration of atoms formed by the action of light has been obliterated. Ultimately, persistent overdevelopment produces one completely black mass of metallic silver.

15.31 Quantum yield of the elementary photographic process. In a general way there is also agreement on another point. The photographic primary process is the extrusion of an electron from a halogen ion. The halogen atom so formed, or some other atom formed by the overall reaction



may react with the gelatin of the emulsion, and thus prevent the possibility of a back reaction



and increase the quantum yield of the photographic process.

Any means which serves to remove halogen atoms from the environs of the primary process and fixes them so that they cannot react in a back reaction increases the photographic sensitivity to light of low intensity. Thus, for

¹⁶ In thallous bromide photography (see § 6.4), the latent image is replaced by a silver latent image before the plate can be developed.

example, anything which promotes diffusion of bromine from the interior of the crystal to the outside has such an effect. Diffusion is slower, the more compact the grain. It occurs less readily in a large, hard grain than in a small, soft one. Hartung¹⁷ measured the process directly by determining the loss in weight of an illuminated thin layer of silver bromide supported on a quartz plate. Koch and Kreiss¹⁸ performed similar experiments on very fine particles ($\sim 3 \times 10^{-5}$ cm. diameter) suspended in air.¹⁹ In these cases the high distribution gradient (of bromine) in the extremely thin crystal layers promoted the diffusion. Were the layers larger and more compact, only a very small amount of bromine would be liberated for the same amount of light absorption.

The distribution gradient can be increased by removing the bromine atoms from the outer layer of the crystal just as soon as they arrive there. Gelatin, as has already been mentioned, has such a function.²⁰ Feldmann and Stern²¹ showed that the quantum yield of photolysis of precipitated silver halides can be increased in the presence of sodium nitrite, which serves to fix the halogen. Some comparisons of quantum yields of the elementary photographic process, compiled in part by Eggert and Noddack,²² are shown in Table 28 (p. 392).

15.32 Sensitivity of the grain. Eggert and Noddack²³ also made the interesting observation that, on the average, a grain must absorb 100 quanta to become developable; i.e., in an emulsion 100 quanta must be absorbed per grain to make half of them developable. In a sensitive emulsion there are a small number of grains (about 1 per cent) which are sensitive to one or two quanta;¹⁴ other grains may be developable without exposure, thus fogging the plate.

¹⁷ Hartung, *J. Chem. Soc.*, **125**, 2198 (1924).

¹⁸ Koch and Kreiss, *Z. Physik*, **32**, 384 (1925).

¹⁹ Cf. R. Schwarz and Stock, *Z. anorg. allgem. Chem.*, **129**, 41 (1923).

²⁰ Cf. Urbach, *Science ind. phot.*, [2] **6**, 288 (1935); *Chimie & industrie*, **35**, 380 (1936).

²¹ Feldmann and Stern, *Z. physik. Chem.*, **B26**, 45 (1934).

²² Eggert and Noddack, *Z. Physik*, **58**, 861 (1929).

²³ Eggert and Noddack, *Handb. wiss. Photographie*, **5**, 263 (1932).

TABLE 28
QUANTUM YIELD OF THE ELEMENTARY PHOTOGRAPHIC
PROCESS

Substance	Condition	Added Agent	γ	Method of Measurement	Reference
AgBr	Compact.	—	<0.01	—	(1)
	Crystal.	—	0.4	Optical (§ 6.33).	(2)
	Crystal.	—	0.18	Dielectric constant.	(11)
	Crystal at 3650 Å.	NaNO ₂	0.4	Chemical.	(7)
	Ppt. moist (no binding agent).	—	0.1	Ag determination.	(4)
	Ppt. moist (no binding agent).	—	0.1	Br determination.	(5)
	Ppt. moist (no binding agent) at 3650 Å.	—	0.4	Ag determination.	(7)
	Ppt. moist (no binding agent) at 3650 Å and 4360 Å.	NaNO ₂	1.0	Ag determination.	(7)
	Gelatin emulsion.	—	~1	Ag determination.	(9)
	Gelatin emulsion.	—	~1	Br determination.	(10)
AgCl	Crystal at 3130 Å.	—	0.13	Ag determination.	(7)
	Crystal.	—	0.33	Optical (§ 6.33).	(2)
	Crystal.	—	0.34–0.58	Optical (§ 6.33).	(3)
	Crystal at 3130 Å.	NaNO ₂	0.20	Ag determination.	(7)
	Ppt. moist (no binding agent) at 3130 Å.	NaNO ₂	1.0	Ag determination.	(6), (7)
	Gelatin emulsion.	NaNO ₂	~1	—	(8)
		<1 part			

REFERENCES

- (1) Eggert and Noddack, in *Proc. VIIth Internat. Congr. Phot.*, W. Heffner & Sons, Cambridge (England), 1929.
- (2) Hilsch and Pohl, *Z. Physik*, **64**, 606 (1930).
- (3) Hecht, *ibid.*, **77**, 235 (1932).
- (4) Kieser, *Z. wiss. Phot.*, **26**, 1 (1928).
- (5) Mutter, *ibid.*, **26**, 193 (1928).
- (6) Feldmann, *Z. Physik. Chem.*, **B12**, 443 (1931).
- (7) Feldmann and Stern, *ibid.*, **B26**, 45 (1934).
- (8) Luther and Weil, *Z. Elektrochem.*, **32**, 500 (1926).
- (9) Eggert and Noddack, *Sitzb. kgl. preuss. Akad. Wiss.*, 631 (1921).
- (10) Dieterle, in *Proc. VIIth Internat. Congr. Phot.*, W. Heffner & Sons, Cambridge (England), 1929, p. 39.
- (11) Martens, *Z. Physik*, **103**, 217 (1936).

Presumably a certain minimum number of electrons must be produced per grain in order that a developable nucleus can be formed and that the back reaction cannot be a serious factor in destroying the latent image.

This result does not mean that, on the average, a developable nucleus requires 100 silver atoms. It is possible that the developable nucleus is much smaller and that the first few electrons produced are not even effective in producing silver atoms. In fact, it is possible that, for this reason, the back reaction at sufficiently low light intensities may counterbalance the forward reaction, thus yielding no developable image no matter how long the exposure. The requirement of a minimum amount of light absorption per grain may perhaps be attributed to the necessity for a minimum electron density within the crystal before a potential hump in the vicinity of the focus of disturbance is exceeded. When the potential rises sufficiently high, the electrons pass to the focus and the discharge of the silver ions commences. From another point of view, the electrons pass rather readily toward the focus, but then there must be a sufficient concentration of electrons there (a sufficiently dense electron atmosphere) to attract the silver ions before the developable nucleus begins to grow.

The *sensitivity specks* of Sheppard are of interest in this connection. They are supposed to be specks of silver sulfide adhering to the grain. The function of the silver sulfide would be to produce foci of disturbance at which the potential hump to be overcome is less. Either the electrons pass more readily, or the silver ions are attracted by a smaller concentration of electrons, depending on the model used to explain the phenomenon.

Photographic emulsions are ripened to make them more sensitive. It is generally believed that this ripening process results in the formation of silver nuclei within the grains. They cannot be at the surface of the grains, because the emulsion would then be developable without exposure. According to Gurney and Mott,¹⁴ such bits of silver are not available as foci for the growth of developable nuclei,

because the pressure produced by the growth of nuclei cannot be relieved within the grain. They grow only at the surface, where the pressure may be relieved by extrusion. In the vicinity of a silver nucleus within the grain, there is assumed, however, to be an electron atmosphere (cf. the potential hump near a nucleus, already mentioned). If the silver nucleus is sufficiently near to a silver sulfide speck, its already available electron atmosphere serves to lower the potential hump at the latter. Thus an ultra-sensitive grain will be one in which a sensitive speck is situated near a bit of silver embedded in the halide. Gurney and Mott suggest that, according to this model, the superior speed of a coarse-grained emulsion is due to the fact that, with increased surface area of the grain, there is an increased probability of such a state of affairs.

15.33 Conditions of precipitation of the halide. It has already been shown that sensitivity to light of low intensity may be increased in two ways. Extremely fine grained emulsions may possess an advantage due to the high concentration gradient of bromine atoms within the grain, thus facilitating their fixation by the gelatin and decreasing the probability of back reaction. We might imagine that such an emulsion will be of value in processes where prolonged exposure to extremely weak light is required. On the other hand, the coarse-grained, ripened emulsions are very much more rapid. On the average, a smaller number of quanta absorbed per grain is required to produce a developable image. Explanations suggested for this phenomenon have already been discussed (§ 15.31).

There is, however, another way in which the sensitivity of an emulsion may be increased. It is important in photography to extend the range to longer wave lengths. Fajans²⁴ pointed out that there is a simple explanation for the well-known fact that the conditions of precipitation of the bromides have a bearing on the photosensitive range. When the silver bromide is precipitated in an excess of silver nitrate,

²⁴ Fajans, *Z. Elektrochem.*, **28**, 499 (1922); Fajans and Frankenburger, *Z. physik. Chem.*, **105**, 255, 273 (1922); Fajans and Steiner, *ibid.*, **125**, 275 (1927).

the positively charged colloidal particles are coated with a layer of adsorbed silver ions. In an excess of halide, the particles are negatively charged and are coated with halide ions. The former are yellower than the usual halide particles; the latter are whiter. The former are sensitive at longer wave lengths. The absorption spectrum of the crystal has been shifted in one way or another, depending on the particular type of strain produced at the surface.

15.34 Sensitive dyes. The range of spectral sensitivity of a photographic plate is actually the range of photochemical sensitivity of the halides. As we have just seen, the latter may be modified slightly by the conditions of precipitation, and it is possible also that the presence of the gelatin substrate may produce strains which will also shift the photosensitive range.²⁵

A much more profound effect, however, may be produced by the introduction, into the emulsion, of dyes which absorb in the particular wave-length region desired. The dyes generally used are found among the cyanines, merocyanines, and acid dyes of the fluorescein series.²⁶ They possess the faculty of absorbing light energy and transmitting it to the halide grain, producing photolysis in a light range where the halide by itself is insensitive. The range of sensitivity thus produced is not identical with that of the dissolved dye. The simplest explanation is that the dye adsorbed at the surface of the grain is also under strain and that its own absorption spectrum is thus modified. Of course, only the adsorbed dye is effective as a photosensitizer. As in other cases of photosensitization (see Chapter X), the dye is not itself permanently affected by the light absorbed. However, one dye molecule can be effective in causing the production of as many as 50 atoms of silver.^{27, 14}

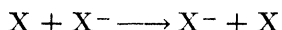
It is improbable that a single molecule should make

²⁵ For a discussion of the orientating effect of the substrate and consequent response to particular planes of polarization, see § 6.5.

²⁶ A desensitization phenomenon usually accompanies sensitization. A good sensitizer gives a minimum of desensitization.

²⁷ Cf. Lescyuski, *Z. wiss. Phot.*, **24**, 261 (1926). Note also that excess of dye causes decrease of sensitivity and lack of contrast.

contact with so many halogen or silver ions at one time, and, accordingly, many models have been devised to explain what takes place. For example, the energy may be transferred directly from the dye to an adjacent halogen ion which thereupon loses an electron, which migrates to some focus of disturbance and ultimately reacts to form a silver atom. The bromine atom is locked within the grain by the dye and cannot escape from its position. However, by a series of reactions of the type



it ultimately regains its charge and some atom produced in a more remote spot is lost from the grain and fixed in the gelatin. The first halogen ion thus again becomes available for absorbing energy from the dye molecule and can, as a result, act as the intermediary for the production of many atoms of silver.

According to another model¹⁴ the potential relationships are such that an activated dye molecule may lose an electron directly to the halide grain, whereupon it functions in the production of a latent image particle (perhaps according to one of the models already described in §§ 6.31, 15.3). The extrusion of the electron from the dye into the grain forces a halide ion out of the grain into the gelatin. The dye molecule recovers its charge from the gelatin-halide ion combination, and the halogen atom is fixed by the gelatin. Thus this model also accounts for the production of many silver atoms by one molecule of dye.

Leermakers, Carroll, and Staud^{27a} have reported an interesting effect in photosensitization. They found that as the concentration of dye is increased, until there is sufficient present for the formation of a unimolecular layer on the silver halide crystals, there is a sharp increase in photosensitivity in a limited range *not* characteristic of the absorption spectrum of the unassociated dye.^{27b}

^{27a} Leermakers, Carroll, and Staud, *J. Chem. Phys.*, **5**, 878 (1937). Cf. *ibid.*, **5**, 893 (1937); Leermakers, *ibid.*, **5**, 889 (1937).

^{27b} For a discussion of the absorption characteristics of dyes under varying conditions, cf. Scheibe, Kandler, and Ecker, *Naturwissenschaften*, **25**, 75 (1937);

15.4 Photosynthesis. It would be imprudent, not to say impudent, to attempt to cover the subject of photosynthesis in the limited space available in a book such as this.²⁸ There follows, instead, a brief outline of the nature of photosynthesis and some of the problems involved, and a brief resume of the methods used and the results obtained by photochemists in an effort to solve those problems.

15.41 Nature of photosynthesis. The term *photosynthesis* is usually applied to the fixation of carbon dioxide and water by light, the final product being of the form of a sugar. The power of such fixation seems to be restricted to living vegetable matter;²⁹ chlorophyll and related dyes, when located in their natural habitat (living leaf, algae, bacteria, etc.), act as photosensitizers for the process. There are, of course, intermediate stages in that fixation, and there is likewise evidence³⁰ that other substances (e.g., acetates, lactates, citrates, and butyrates) may be used as starting points for the photosynthetic process. Furthermore, we must not ignore the fact that there are other photosynthetic processes in which the initial reactants are quite different. The green and purple sulfur bacteria, for example, consume carbon dioxide and hydrogen sulfide in the light, the latter substance yielding sulfur and sulfuric acid.³¹

In the purple bacteria, infrared light between 9200 and 7500 Å is effective in producing photosynthesis. In the more common types of photosynthesis with which we are ordinarily concerned, the threshold of activity is at 7000 to 6600 Å,³² and 6800 Å is the longest wave length at which

Jelley, *Nature*, **138**, 1009 (1936); **139**, 631 (1937); Bloch and Hamer, *Phot. J.*, **59**, 21 (1928).

²⁸ For a discussion of the background of this subject, the reader is referred to Spoehr, *Photosynthesis*, Reinhold Publishing Corp., New York, 1926.

²⁹ Cf. § 15.5, for attempts at photosynthesis in vitro.

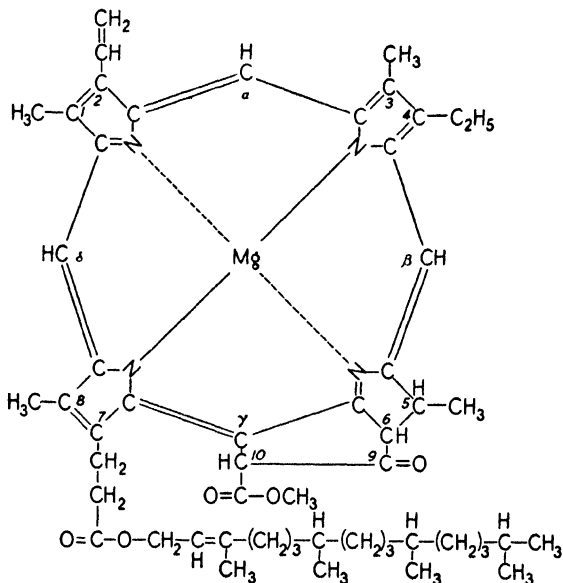
³⁰ Treboux, *Ber. deut. botan. Ges.*, **23**, 432 (1905). Bokorny, *Biol. Zentralbl.*, **17**, 5 (1897). Loew and Bokorny, *J. Prakt. Chem.*, **144**, 272 (1887). *Chemie der Zuckerarten*, vol. II, p. 1763 (1904). Cf. Spoehr, *op. cit.*, p. 297.

³¹ Cf. Van Niel, *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 138 (1935).

³² (a) Spoehr, *op. cit.*, p. 118; (b) Hoover, *Smithsonian Misc. Coll.*, No. 21 (1937).

the quantum yield has actually been determined. It is the limit for photosynthesis only in very thin layers of chlorophyll; in thick layers the few thermally excited molecules account for photosynthesis beyond 6800 Å.³³

Chlorophyll occurs in the green plant in two forms: chlorophyll *a* ($C_{55}H_{72}N_4O_6Mg$), which is said to have the structural formula shown below;³⁴ and chlorophyll *b*



($C_{55}H_{70}N_4O_6Mg$), in which the methyl group in position 3 of the above formula is replaced by the formyl group $-CHO$. In most plants the ratio is $a : b = 3 : 1$. The formation of chlorophyll in plants appears to occur via a photochemical process; the parent substance, protochlorophyll, is itself colorless.³⁵

The absorption spectra of the two chlorophylls are indicated graphically in Fig. 57, according to Zscheile.³⁶

³³ Cf. G. R. Burns, *J. Phys. Chem.*, **41**, 308 (1937).

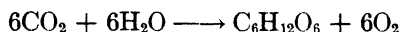
³⁴ Fischer, *Chem. Rev.*, **20**, 41 (1937); cf. Steele, *ibid.*, **20**, 1 (1937).

³⁵ Cf. Rothemund, *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 71 (1935).

³⁶ (a) Zscheile, *Botanical Gazette*, **95**, 529 (1934); (b) *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 108 (1935).

The fluorescence bands of the excited chlorophylls are shown in Fig. 58 (p. 400).^{36b, 37}

The overall reaction for photosynthesis is usually written:



The basis for this reaction is twofold: the volumes of CO_2

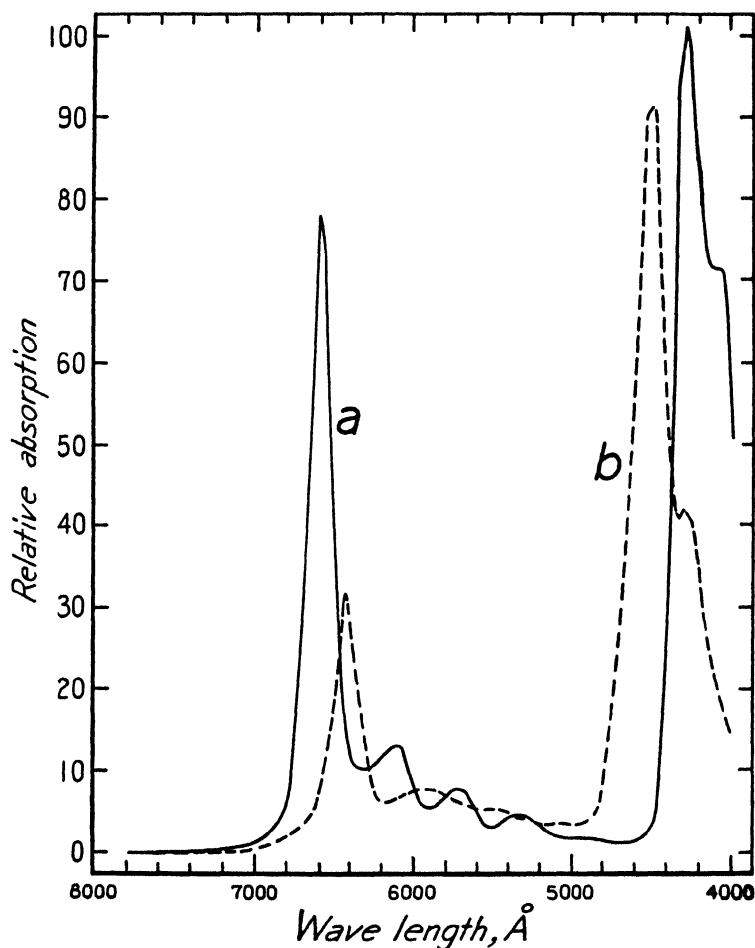


Fig. 57. Absorption Curves for the Two Chlorophylls, according to Zscheile, *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 108 (1935).

³⁷ Zscheile, *Protoplazma*, **22**, 513 (1935).

absorbed and O_2 emitted during respiration are very nearly equal, and hexoses occur very commonly in leaves.³⁸ Contrarily, according to Kostytschew,³⁹ the amount of O_2 emitted is considerably less than that of CO_2 absorbed during the first few minutes, the ratio attaining unity after 15 to 30 minutes. However, even though the $O_2 : CO_2$ ratio

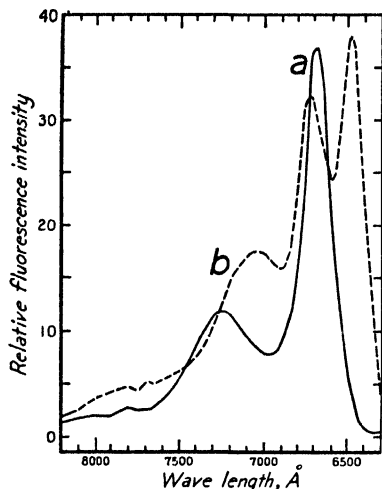


Fig. 58. Fluorescence Bands of the Excited Chlorophylls Dissolved in Ether, according to Zscheile, *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 108 (1935).

is less than unity at the beginning, the evidence indicates that the production of O_2 is observed immediately, even for light of low intensities.⁴⁰

15.42 Products of photosynthesis. It has already been mentioned that hexoses are a common component of living leaves, and for this reason a sugar of the form $C_6H_{12}O_6$ is usually set up as the final stage of the photosynthetic process. However, on theoretical grounds (if on no other), we are forced to assume the existence of intermediate stages. Most of the mechanisms proposed have sug-

gested the intermediate formation of formic acid and formaldehyde, the latter polymerizing via a photochemical (cf. § 13.6) or catalytic process to give a hexose. As is readily apparent, however, glycolic aldehyde ($CH_2OH \cdot CHO$) might also be an intermediate for the formation of a hexose. One possible test of a proposed mechanism is the detection, in the living plant (leaf, algae, or bacteria, etc.), of the intermediates suggested. Many of the investigations (of the

³⁸ Spoehr, *op. cit.*, p. 156. See, however, § 15.49.

³⁹ Kostytschew, *Ber. bot. Ges.*, **39**, 319 (1922).

⁴⁰ Warburg, *Über die Katalytischen Wirkungen der Lebendigen Substanz*, Julius Springer, Berlin, 1928.

organic chemists, in particular) have been bent in that direction.

The existence of formaldehyde in living leaves is subject to serious question.⁴¹ None of the evidence so far produced seems to be reliable. Glycolic aldehyde has also been suggested as an intermediate, but here again there is no conclusive evidence as to its actual existence in the leaf. On the other hand, although glyoxylic acid ($\text{CHO} \cdot \text{COOH}$) has been reported by several investigators,⁴² there is no evidence that it is actually associated with the process of photosynthesis. Similar statements apply to the presence of glycolic acid (HOCH_2COOH), which is found in a wide variety of plants, in both the leaves and the fruit.⁴³ Although formic acid is usually assumed as an intermediate, there is in this case also serious question as to its occurrence, especially in leaves;⁴⁴ however, there is little doubt as to the presence of oxalic acid, $(\text{COOH})_2$.

Among the carbohydrates found in plants are one containing three carbon atoms⁴⁵ (in cabbage leaves), and many pentoses. The latter are usually found in the combined form as pentosans and may be either dextrorotatory or levorotatory. The hexoses found in plants are restricted to only a few of the 32 possible isomeric aldohexoses, 2-ketohexoses, and 3-ketohexoses. Of those found, all are dextro compounds.

15.43 Locus of photosynthesis. Photosynthesis has been observed only in cells containing chlorophyll; the albino parts of the leaf are without effect. During the process the amount of chlorophyll is unchanged.⁴⁶ Photosynthesis takes place, not throughout a whole cell, but apparently

⁴¹ Spoehr, *op. cit.*, p. 289.

⁴² Brunner and Chuard, *Ber. chem. Ges.*, **19**, 595 (1886); Lippman, *ibid.*, **24**, 3299 (1891); Talladin, *Bull. acad. sci. (Petrograd)*, 1021 (1916).

⁴³ Gorup-Besanez, *Ann. Chem.*, **161**, 223 (1872); Shorey, *J. Am. Chem. Soc.*, **21**, 45 (1899); Stolle, *Chem. Zentr.*, **4**, II, 343 (1900); Ordonneau, *Bull. soc. chim.*, [3] **6**, 261 (1891).

⁴⁴ Spoehr, *op. cit.*, p. 292.

⁴⁵ Buston and Schryver, *Biochem. J.*, **17**, 470 (1923).

⁴⁶ Willstätter and Stoll, *Untersuchungen über die Assimilation der Kohlen-säure*, Julius Springer, Berlin, 1918.

only in certain, well-defined, small bodies within the cytoplasm. These minute bodies, the chloroplasts, contain the chlorophyll. They are of variable number, shape, and size, depending on the plant.⁴⁷ Among investigators there is disagreement as to whether the chlorophyll is distributed uniformly throughout the chloroplast or located only on the surface. Statements have been made⁴⁸ that, when chloroplasts are removed from the cells in which they are contained, they continue their photosynthetic activity for some time.

Chlorophyll shows the same absorption spectrum in colloidal solution in water as in the living leaf. Willstätter and Stoll⁴⁶ have concluded consequently that it exists in the colloidal form in the latter. This appears to be contrary to the fact that chlorophyll in the leaf exhibits fluorescence, a phenomenon characteristic only of its true solutions (i.e., of the molecularly dispersed form). Neither solid chlorophyll nor colloidal solutions show any fluorescence.⁴⁹ Franck and Herzfeld⁵⁰ have adopted the view that the chlorophyll is adsorbed on the surfaces of the chloroplasts, which are themselves colloidal particles.

It is interesting that leaves which have been killed by freezing or by drying for a long time (up to three months) still yield oxygen when moistened and exposed to light. Etiolated leaves (leaves in which, due to development in the dark, chlorophyll has not been formed) do not possess this property. According to Molisch,⁵¹ leaves which had been heated to 84° for five hours still showed a capacity for photosynthesis in the moist condition; but, when leaves were heated to 96° for one hour, this capacity was destroyed. Treatment with ether in the course of the drying operation

⁴⁷ For a discussion of the structure of the chloroplasts, cf. Spoehr, *op. cit.*, p. 380.

⁴⁸ Englemann, *Bot. Zeitg.*, **39**, 446 (1881). Ewart, *J. Linnean Soc.*, **31**, 364 (1896); *Bot. Centralb.*, **72**, 289 (1897); **75**, 33 (1898). Cf. Kay, *Ber. bot. Ges.*, **15**, 388 (1897); *Bot. Centralb.*, **73**, 426 (1898); Kostytschew, *Ber. bot. Ges.*, **39**, 333 (1921).

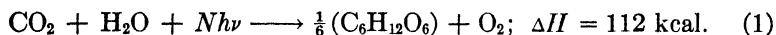
⁴⁹ Stern, *Ber. bot. Ges.*, **38**, 281 (1920); *Zeit. Bot.*, **13**, 193 (1921).

⁵⁰ Franck and Herzfeld, *J. Chem. Phys.*, **5**, 237 (1937).

⁵¹ Molisch, *Bot. Zeitg.*, **62**, 1 (1904).

had a similar effect. It seems that any factor severe enough to change the normal distribution of chlorophyll on or in the chloroplasts (which may be oily or lipid particles), or to cause its agglomeration into particles of greater than molecular dimensions, ends the photosynthetic capacity; that this capacity is not dependent on "life" within the leaf; and that it is a joint characteristic of the chlorophyll molecules and the chloroplasts to which they are attached.

15.44 Quantum yield. The reaction



can be produced in the living leaf by light of 7000 Å, corresponding to only 38 kcal. Thus, the "energetically permissible" quantum yield cannot exceed 38/112, or 0.34. However, as we shall see, it is unlikely that this maximum should be achieved since there is at least one exothermic step in the process. Furthermore, the absorption of light by plant material other than chlorophyll would tend to lower the yield.

The highest yield so far reported is that of Warburg and Negelein.⁵² Working with algae cultivated so that no excess of chlorophyll would be present, and in an excess of carbon dioxide, they obtained values of practically 0.25 at wave lengths of 6600 Å (red), 5780 Å (yellow), and 5461 Å at 10°C. In the region at 4360 Å (blue), the process seemed slightly less efficient (~ 0.2).

The attempts of other investigators to duplicate those high quantum yields have been generally unsuccessful. A very careful series of investigations conducted by the Wisconsin group⁵³ over a period of five years have failed to indicate quantum yields in chlorella in excess of ~ 0.06.^{53a}

⁵² Warburg and Negelein, *Z. physik. Chem.*, **106**, 191 (1923).

⁵³ Manning, Stauffer, Duggar, and Daniels, *J. Am. Chem. Soc.*, **60**, 266 (1938); Manning, Juday, and Wolf, *ibid.*, **60**, 274 (1938).

^{53a} The quantum yield of this reaction was extensively discussed at the Stanford University Symposium on the Photochemistry of Polyatomic Molecules (Aug. 9-11, 1938). By making a suitable correction for respiration, Daniels has obtained a value of ~ 0.07 depending on environmental conditions and previous history of the algae. Measuring the photosynthesis by a radiometer method, Arnold obtained evidence which indicates that less than eight

They have concluded that attempts to formulate a specific mechanism for photosynthesis, with identifiable intermediate compounds, are only justifiable and profitable if the higher quantum yields are the true ones; but that, if their own values are the true maxima, the possibilities for energy dissipation by side reactions, deactivation of chlorophyll, and inefficient forward steps in the process become so numerous as to make the number of energetically possible mechanisms very large.

However, in any consideration of possible mechanisms, it is necessary to account for the highest quantum yield reported. The mechanism must not be such as to be unallowable at that quantum yield. Furthermore, it would seem offhand that the possible errors are such as to decrease the apparent quantum yield rather than to increase it. Such errors may be introduced by failure to make contact between CO_2 and the light-absorbing chlorophyll, by lack of opportunity for respiration, and by absorption by other constituents of the reaction mixture. That the value of 0.25 for the quantum yield is directly related to a fundamental mechanism of some kind is indicated by the work of Roelofsen⁵⁴ on the quantum yield of photosynthesis in purple bacteria (in which H_2S is involved). In that case one quantum would fulfill the energy requirements. Nevertheless, it is found that here, also, four quanta are absorbed per CO_2 molecule converted. It is interesting to note in this connection that investigations on the chemistry of "bacteriochlorophyll" have shown that it is chemically closely related to chlorophyll.⁵⁵

quanta (i.e., $\gamma > 0.125$) are required to fix one molecule of CO_2 . According to Franck, Rieke has repeated the experiments of Warburg and Negelein and has succeeded in reducing the number of quanta required to fix one molecule of CO_2 to ~ 4.5 (i.e., $\gamma \approx 0.22$). Publications detailing the experimental evidence are probably to be expected at about the same time as the publication of this book.

⁵⁴ Roelofsen, Thesis, Utrecht, 1935. Cf. Van Niel, *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 138 (1935).

⁵⁵ Noack and E. Schneider, *Naturwissenschaften*, **21**, 835 (1933); Schneider, *Z. physiol. Chem.*, **226**, 221 (1934); Fischer and Hasenkamp, *Ann.*, **515**, 148 (1935); Clemo and McIlwain, *Chem. and Ind.*, **54**, 135 (1935).

15.45 Blackman reaction. Above certain high concentrations of CO_2 or intensities of light, increase of either of these factors does not augment the rate of photosynthesis. Under such conditions, on the other hand, increase of temperature from 15° to 25° causes the rate of photosynthesis to double.⁵⁶

According to Warburg, these facts indicate that, in the mechanism of carbon dioxide reduction, a slowly progressing chemical reaction plays a role and limits the rate of photosynthesis.⁵⁷ This reaction Warburg called the *Blackman reaction*. When the light intensity is low, the temperature coefficient of the fixation of CO_2 is low, as is usually the case in simple photochemical reactions. The high temperature coefficient at high light intensities is characteristic of a thermal or *dark* reaction; it is the latter which puts the limit on the rate of photosynthesis.

15.46 Fluorescence.⁵⁸ When leaves are strongly illuminated in the presence of oxygen, they emit fluorescent light with an intensity which changes with time of irradiation.⁵⁹ In the first second, the intensity reaches a maximum and falls off slowly to a stationary value. An explanation for these phenomena has been given by Franck and Wood,⁵⁹ who suggest that, during the dark period prior to illumination, the chlorophyll adsorbs plant acids. On illumination these plant acids use the energy absorbed by the chlorophyll (in a photosensitized reaction) either for photosynthesis or for photo-oxidation. In either event, the energy absorbed is not reemitted as light and the fluorescence in the first moment of illumination is weak. According to Franck and Herzfeld,⁶⁰ these plant acids enter into reactions in which complexes are produced that cannot proceed with photo-

⁵⁶ Blackman and Smith, *Proc. Roy. Soc. (London)*, **B83**, 389 (1911).

⁵⁷ Warburg, *Biochem. Zeit.*, **100**, 230 (1919); **103**, 188 (1920); *Naturwiss.*, **9**, 354 (1921). Warburg and Negelein, *Z. physik. Chem.*, **102**, 235 (1922); **106**, 191 (1923). Warburg and Vyeseige, *Biochem. Zeit.*, **146**, 486 (1924).

⁵⁸ See Fig. 58 for the fluorescence spectra of the two chlorophylls dissolved in ether.

⁵⁹ Cf. Franck and Wood, *J. Chem. Phys.*, **4**, 551 (1936), who have reviewed the literature and made a thorough study of this phenomenon.

⁶⁰ For a more detailed discussion, see § 15.48.

synthesis until certain groupings are restored. These short-lived complexes are strong emitters of radiation, and the fluorescence consequently rises at first. The decay of fluorescence following the maximum may be attributed to consumption of the plant acids.

15.47 Photosynthetic unit. The principal way in which photosynthesis has been believed to differ from the photochemical reactions with which we are generally familiar was in the existence of the *photosynthetic unit*. In this unit a large number of molecules are supposed to cooperate in a way not encountered in vitro.^{12a} The name is given to a group of about 1000 chlorophyll molecules connected with one carbon dioxide molecule. In this unit the chlorophyll molecules are presumed to absorb light practically independently of each other, but all the energy absorbed by any part of the unit is supposed to be available for the fixation of the single carbon dioxide molecule. The hypothesis was devised to explain three different sets of experiments.

(1) There is no delay in the production of oxygen at low light intensities.⁴⁶ If it is assumed that one CO₂ molecule is associated with a single chlorophyll molecule and that four quanta must be absorbed for the production of one O₂ molecule, then that O₂ molecule would not be liberated until the chlorophyll had absorbed the required four quanta. The time required for this absorption, with the light intensities used, is sufficient so that a delay in the appearance of oxygen should be noted. On the other hand, if 1000 chlorophyll molecules were associated with the single CO₂ molecule, the time required would be reduced by a factor of 1000 and would be difficult to detect.

(2) Light saturation occurs in the presence of CO₂ at a light intensity⁶¹ much smaller than expected. The saturation has been attributed to the presence of a dark reaction (the Blackman reaction; see § 15.45). At sufficient light intensity the dark reaction would become the slowest or governing reaction and thus limit the rate of the whole sequence to its own speed. It has been stated that the speed

⁶¹ Emerson and Arnold, *J. Gen. Physiol.*, **16**, 191 (1932).

determined for this reaction turns out so large as to necessitate the absorption of four quanta by a unit of 1000 chlorophyll molecules with the conversion of a single CO_2 molecule.

(3) In Emerson and Arnold's investigations with light flashes of very short duration,⁶¹ the dark pauses between flashes (if long enough) allow the completion of the dark reaction. By changing these intervals, they measured the duration of the dark reaction. Changing the intensity of the flashes, they observed a saturation for the individual flash. The intensity required to produce saturation in such flashes is much less than the intensity required in continuous illumination. According to Arnold,⁶² this fact may be explained by the assumption that all the carbon dioxide associated with the chlorophyll at the beginning of the flash is reduced by one flash and the subsequent dark reaction. A comparison between the amount of oxygen produced by one such flash and the amount of chlorophyll available again gives a ratio of about 1000 chlorophyll molecules to one CO_2 .

The agreement in the value of the ratio calculated in these three ways is good (varying from 500 to 2600) and seems fairly convincing. The main objections advanced have already been cited (§15.43). The evidence on the basis of absorption spectra and fluorescence is contrary to the existence of chlorophyll agglomerates. Franck and Herzfeld⁶⁰ suggest, instead, that the chlorophyll is adsorbed on the surfaces of the chloroplasts. This is in agreement with the accepted picture of colloidal distribution of the chlorophyll in the leaf, and at the same time permits the individual chlorophyll molecules to be separated.

The last is an important consideration. According to Prins,⁶³ the yield of fluorescence in all (true) organic solutions of chlorophyll is rather small. Such a result can be attributed only to one of two rapid reactions: a decomposition of the molecule itself, or a reaction with the organic solvent (e.g., a simple deactivation). Franck and Herzfeld

⁶² Cf. Arnold, *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 124 (1935).

⁶³ Prins, *Nature*, **134**, 457 (1934).

have stated that, in an exaggerated case where 1000 chlorophyll molecules are closely associated in a single unit, they would expect the major portion of the energy to be consumed in reactions between the chlorophyll molecules. They also have called attention to the fact that, under suitable illumination, organic solutions of chlorophyll containing oxygen show a type of dependence of fluorescence on time similar to that shown by Kautski⁶⁴ for the living leaf, the time scale only being different.⁶⁵ This result suggests the same kind of state in the two cases, i.e., molecular dispersion.

15.48 A model for photosynthesis.⁶² We have already seen (§15.42) that the effort to isolate formic acid and formaldehyde (two compounds generally assumed to be intermediates) from the living leaf have been generally unsuccessful. It would seem as if, at the present time, we are without the most elementary means by which to test any proposed mechanism. Nevertheless, the development of such a mechanism is of much more value than a mere exercise in ingenuity. It is important, from the point of view of the physicist and the chemist, to show that a mechanism can be devised to explain all the facts we now know, without any departure from the commonly accepted laws relating to photochemical processes. Such a mechanism is subject to revision as our knowledge of the photosynthetic process grows. Its value is not as a complete structure but as a scaffolding, subject to alteration, on which we can hang our ideas. In proposing the mechanism, a brief resume of which follows, Franck and Herzfeld emphasized precisely the points just discussed.

To begin with, Franck and Herzfeld assume that the saturation is due to a back reaction initiated by light and proceeding via chains.⁵⁰ Previously⁶⁶ they had shown that, when a molecule possesses twelve useful (i.e., vibrational) degrees of freedom, the energy from those degrees of freedom

⁶⁴ Kautski and co-workers, *Naturwissenschaften*, **19**, 964, 1043 (1931); **24**, 317 (1936); *Ber.*, **65**, 1762 (1932); **66**, 1588 (1933); **68**, 152 (1935); *Biochem. Zeits.*, **274**, 423 (1934); **278**, 373 (1935); **284**, 412 (1936).

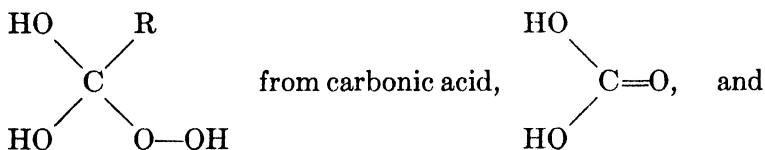
⁶⁵ Franck and Levi, *Z. physik. Chem.*, **B27**, 409 (1935).

⁶⁶ Franck and Herzfeld, *J. Phys. Chem.*, **41**, 97 (1937).

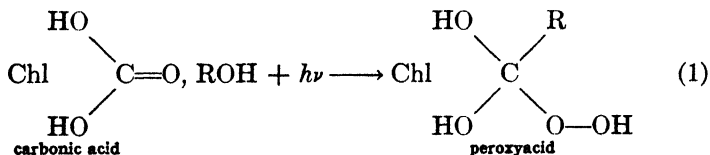
might be contributed to a photochemical process, so that an energy deficiency of ~ 7 kcal. would not interfere with the course of an otherwise possible reaction. It is generally assumed that the oxygen produced in photosynthesis comes from the decomposition of a peroxide. Since the energy deficiency for the formation of H_2O_2 , performic acid,⁶⁷ and formic peraldehyde may be shown to be excessive, they propose, instead, a mechanism involving the formation of a peroxide which needs 5 to 10 kcal. less than does H_2O_2 . The immediate production of O_2 on illumination (§15.41) shows that such a peroxide must be formed in the plant on the absorption of the first quantum. Since the wave length is $\sim 6700 \text{ \AA}$, it seems that the energy required to change H_2CO_3 into this peroxide is ~ 43 kcal. They consequently suggest the following picture.

In the plant the chlorophyll-carbonic acid complex is attached to an organic molecule ROH (present in abundance), in which the strength of the R—OH bond is assumed to be ~ 70 kcal. The ROH may be a protein which forms the main body of the chloroplasts, on the surface of which the chlorophyll is adsorbed. The chlorophyll molecules may move along the surface of the chloroplast as a two-dimensional gas.

The energy required for the formation of the peroxyacid

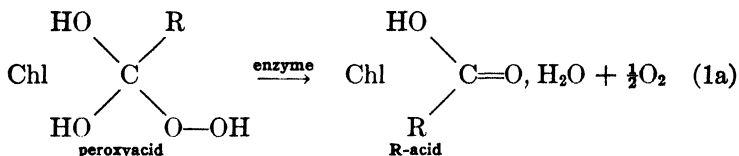


ROH is calculated to be a little smaller than that available from the first absorption act.



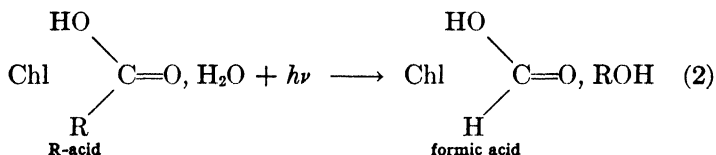
⁶⁷ Cf. Wohl, *Z. physik. Chem.*, **B31**, 152 (1935).

where Chl is a molecule of chlorophyll. This reaction is followed immediately by an enzymatic reaction:

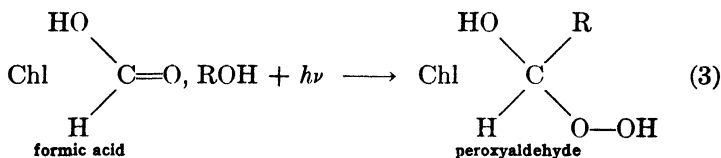


in which the peroxyacid is reduced to an R-acid without the aid of light, thus accounting for the absence of an induction period.

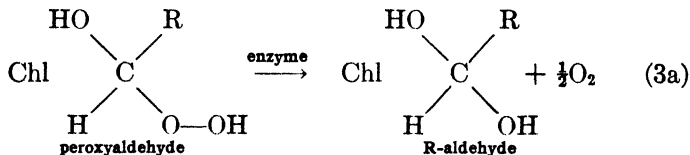
In the next stage, formic acid is produced and the ROH molecule is reformed:



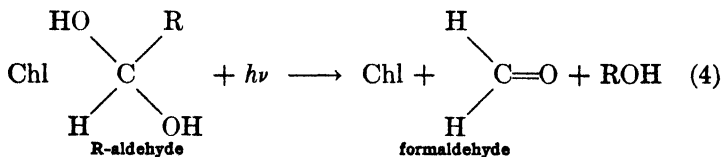
The other reactions are analogous to those we have already seen.



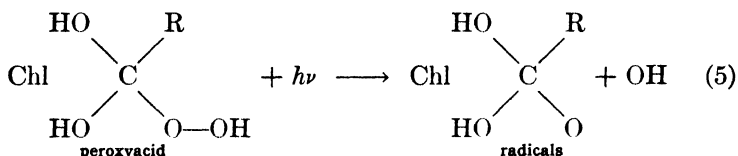
The peroxyaldehyde yields oxygen in an enzymatic (dark) reaction:



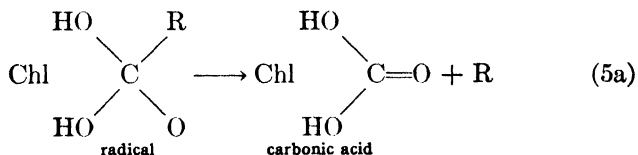
and the R-aldehyde is converted to formaldehyde in the last photochemical step:



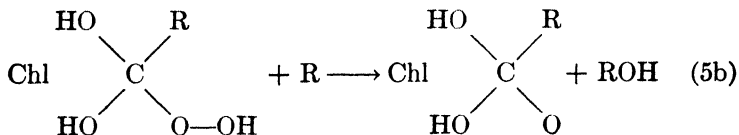
In their paper, Franck and Herzfeld have considered the energy requirements of the reactions in detail. For the sake of brevity we pass over that subject and refer now to the matter of the Blackman reaction (§15.45). It is assumed that absorption of light by a peroxymolecule, unlike the enzymatic changes (1a) and (3a), causes decomposition into radicals which then start chain reactions; these *chain reactions are back reactions* of the peroxyacid to carbonic acid and ROH, and of the peroxyaldehyde to formic acid and ROH. The reactions tentatively suggested for the peroxy-acid are:



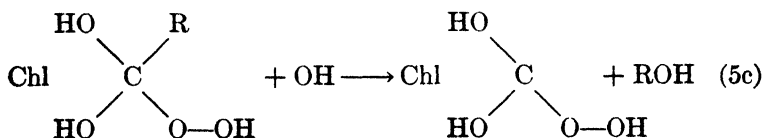
followed by the decomposition of a radical yielding carbonic acid and a new radical:



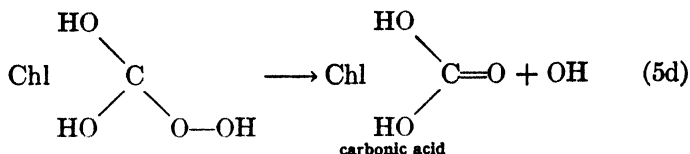
Both the free R and the free OH radicals may initiate chains. Thus



with reaction (5a) repeated thereafter. Or



followed by



with reaction (5c) repeated thereafter.

The chains are, of course, brought to an end by the disappearance of the free R and OH radicals, presumably by their combination. A similar series of reactions may be written for the peroxyaldehyde.

The original paper considers in detail the kinetics of the various possible reactions, as well as photosynthesis starting with plant acids, respiration, and photo-oxidation. We mention briefly the fuller explanation they have given for the course of the fluorescence curves in leaves, discussed by Franck and Wood.

In the dark pause prior to illumination, the chlorophyll molecules have adsorbed plant acids which can use the absorbed light either for photo-oxidation or for photosynthesis, thus reducing the initial intensity of the fluorescence. A chain reaction of *photo-oxidation* produces radicals in the side branches of the plant acids. These radicals may react with ROH molecules instead of with oxygen. Cf. reactions (5b) and (5c). Such a reaction breaks the chain and forms a short-lived complex which is unable to proceed with photosynthesis until the ROH is restored; the absorbed light is not used for photochemical purposes and is consequently reemitted as fluorescence. The production of the complexes gives the rise of the fluorescence curves; the decay of the fluorescence curves is due to the consumption of plant acids.

One other interesting point involves the fact that the same process of photosynthesis is induced irrespective of the color of the light with which the chlorophyll is illuminated. It would seem that photochemical reactions caused by short wave length light might be destructive to the plant. Consequently the chlorophyll must possess a mechanism for getting rid of the energy in excess of that corresponding to $\sim 6600 \text{ \AA}$. The possibility of such behavior for polyatomic

molecules has been discussed by Teller,⁶⁸ who showed that, if the molecule is brought into a highly excited state, it may drop quickly into a lower excited state without radiation, the difference in energy being converted into vibration which is ultimately conducted away as heat. That chlorophyll apparently possesses just such a mechanism is indicated by the fact that the color of its fluorescence is always red, even if excited by yellow-green or blue light.

In concluding this section, two points must be emphasized. (1) In the limited space available, we have not done justice to the mechanism proposed by Franck and Herzfeld. (2) Their mechanism, although physically satisfactory, is admittedly sketchy and preliminary, and is subject to considerable revision as our knowledge of the chemistry of photosynthesis increases.

15.49 Photosynthetic studies with radio-carbon. Ruben, Hassid, and Kamen^{69a} have begun a series of investigations in which artificially radioactive C¹¹ (half-life, 21.5 min.) in the form of CO₂ is used in a study of photosynthesis. In this way it is found that barley plants previously etiolated for ~ 10 hr. form appreciable amounts of radioactive carbohydrates, chlorophyll, carotin, and xanthophyll when illuminated for 45 min. The great bulk (~ 85 per cent) of radio-C fixed is water soluble and is probably in the form of amino acids and alcohols. The principal limitation on the method is the short life of radio-C. Presumably, when more intensely radioactive carbon is used, it will be possible to vary the time of illumination and to extend the possibilities of the method.

15.5 Photosynthesis in vitro. The study of the theory and phenomena of natural photosynthesis has been accompanied by a persistent effort to duplicate that photosynthesis in the laboratory. Relatively little success has been claimed. Baly⁶⁹ has reported that he obtained encouraging results by illuminating hydrated CO₂ adsorbed

⁶⁸ Teller, *J. Phys. Chem.*, **41**, 109 (1937).

^{69a} Ruben, Hassid, and Kamen, private communication.

⁶⁹ Baly, *Nature*, **140**, 930 (1937).

on NiO catalyst with white light. An unstable, readily polymerizable carbohydrate is supposed to be formed. By treatment detailed in his report, the polymer is converted into a complex which is described as the apparent parent of starch. However, previous failures by other investigators to duplicate similar supposedly successful photosyntheses *in vitro* have created about the whole subject an atmosphere of skepticism which demands repeated verification by independent investigators before any such claim is accepted.⁷⁰

15.6 Other heterogeneous photochemical reactions. The number of the heterogeneous reactions has been by no means exhausted by the brief reference we have made to them. Unfortunately the available knowledge of most of them is so limited that it would be impractical to attempt to discuss them in this book. We may conclude by saying that the biochemical problems involved in the ultraviolet synthesis of vitamin D, in the reactions of visual purple within the eye, and in phototropism are still on the borderline of photochemical knowledge. Like the subject of photosynthesis, they are goals for the future.

⁷⁰ Cf. Dhar, *Cold Spring Harbor Symposia Quant. Biol.*, **3**, 151 (1935), for a brief review of this subject.

APPENDIXES

APPENDIX I COMPARISON OF NOTATIONS FOR ATOMIC ENERGY STATES

Prior to the development of the present theory of atomic spectra, many different notations were used to designate the *atomic energy levels* or *terms*, as they were usually called by spectroscopists. A complete table of all the notations which appeared in the literature would be inconvenient to use; the table presented here shows the relationship between only the most commonly used notations.

TABLE 29
DICTIONARY OF NOTATIONS FOR ATOMIC STATES

SYSTEM	Lande *	Rydberg-Fowler	Paschen-Sommerfeld	Russell-Saunders	Present Notation
SINGLETs	n_{10}^1	<i>S</i>	<i>S</i>	$^1S_0$	$^1S_0$
	n_{21}^1	<i>P</i>	<i>P</i>	$^1P_1$	$^1P_1$
	n_{32}^1	<i>D</i>	<i>D</i>	$^1D_2$	$^1D_2$
	n_{43}^1	<i>F</i>	<i>F</i>	$^1F_3$	$^1F_3$
DOUBLETs	n_{11}^2	σ	<i>s</i>	^2S	$^2S_{1/2}$
	n_{21}^2	π_2	p_2	$^2P_1$	$^2P_{1/2}$
	n_{22}^2	π_1	p_1	$^2P_2$	$^2P_{3/2}$
	n_{32}^2	δ', δ_2	d_2	$^2D_2$	$^2D_{3/2}$
	n_{33}^2	δ, δ_1	d_1	$^2D_3$	$^2D_{5/2}$
	$n_{4j}^2 (j = 3, 4)$	ϕ	<i>f</i>	^2F_j	$^2F_{j-1/2}$
TRIPLETs	n_{11}^3	<i>s</i>	<i>s</i>	$^3S_1$	$^3S_1$
	n_{20}^3	p_3	p_3	$^3P_0$	$^3P_0$
	n_{21}^3	p_2	p_2	$^3P_1$	$^3P_1$
	n_{22}^3	p_1	p_1	$^3P_2$	$^3P_2$
	n_{31}^3	d'', d_3	d_3	$^3D_1$	$^3D_1$
	n_{32}^3	d', d_2	d_2	$^3D_2$	$^3D_2$
	n_{33}^3	d, d_1	d_1	$^3D_3$	$^3D_3$
	$n_{4j}^3 (j = 2, 3, 4)$	<i>f</i>	<i>f</i>	^3F_j	^3F_j

* In the Lande system, *n* is the principal quantum number. Although there is great variation in the choice of the principal quantum number, it is usually obvious what levels are involved.

APPENDIX II

HEATS OF REACTION AND BOND STRENGTHS

Table 30 is given on p. 419; Table 31, on pp. 420-421; and Table 32, on pp. 422-423.

In Tables 30-32 are gathered some data which may be useful in reading this book and in making *rough* calculations. The values for the heats of dissociation of diatomic elements (Table 30) are fairly well known for all cases listed, except carbon. For carbon, the wide range cited, ~ 90 -161.4 kcal., is indicative of the state of confusion concerning these data. It is suggested that, in any case, the reader refer to the original references when precise calculations are required.

In Table 31, the data listed may sometimes appear inconsistent with figures quoted in the text. In such cases the explanation is simply that the figures given by the authors concerned have been used as a matter of convenience. The differences are never large. However, if further calculations are required, it is advisable for the reader to use the data in the tables exclusively.

In Table 32, the bond strengths suggested by various investigations are listed without comment. A critical examination of the subject is beyond the scope of this book. In making use of such data, it should be remembered that it is necessary to use consistent values. Thus, if one chooses to use the low value for the strength of the C—H bond, he must also use the low value for the C—C bond. A combination of the low value for C—H and the high value for C—C may lead to weird results and untenable conclusions.

TABLE 30

HEATS OF DISSOCIATION OF SEVERAL DIATOMIC ELEMENTS

Element	kcal.	Reference
p-H ₂	102.72 ± .02	(2); cf. (1)
n-H ₂	102.48 ± .02	(2)
HD	103.54 ± .02	(2); cf. (3)
D ₂	104.52 ± .02	(2); cf. (3)
O ₂	116.4	(4); cf. (5)
S ₂	102.6	(6), (7)
F ₂	76 ± 2	(8)
Cl ₂	56.90	(9)
Br ₂	45.23	(10)
I ₂	35.39	(9), (11), (12)
N ₂	169.3	(13)
P ₂	115.45	(14)
As ₂	38	(15)
C ₂	159.62	(16)
	161.4	(17)
	90	(18)

REFERENCES

- (1) Giauque, *J. Am. Chem. Soc.*, **52**, 4816 (1930).
- (2) Beutler, *Z. physik. Chem.*, **B29**, 315 (1935).
- (3) Johnston and Long, *J. Chem. Phys.*, **2**, 387, 710 (1934).
- (4) Knauss and Ballard, *Phys. Rev.*, **48**, 796 (1935).
- (5) Herzberg, *Chem. Rev.*, **20**, 145 (1937).
- (6) Christy and Naude, *Phys. Rev.*, **37**, 903 (1931).
- (7) Montgomery and Kassel, *J. Chem. Phys.*, **2**, 417 (1934).
- (8) Desai, *Proc. Roy. Soc. (London)*, **A136**, 76 (1932).
- (9) Giauque and Overstreet, *J. Am. Chem. Soc.*, **54**, 1731 (1932).
- (10) Gordon and Barnes, *J. Chem. Phys.*, **1**, 692 (1933).
- (11) Gibson and Heitler, *Z. Physik*, **49**, 471 (1928).
- (12) Gordon and Barnes, *J. Chem. Phys.*, **1**, 297 (1933).
- (13) Herzberg and Sponer, *Z. physik. Chem.*, **B26**, 1 (1934). Rasetti, *Phys. Rev.*, **34**, 367 (1929).
- (14) Herzberg, *Ann. Physik*, **15**, 677 (1932).
- (15) Trivedi, *Bull. Acad. Sci., United Provinces Agra Oudh (India)*, **3**, 1 (1933).
- (16) Kelley, *U. S. Bureau of Mines Bull. No. 383*.
- (17) Birge, *International Critical Tables*, McGraw-Hill Book Co., New York, 1929, vol. 5, p. 418.
- (18) Herzberg, Herzfeld, and Teller, *J. Phys. Chem.*, **41**, 325 (1937).

TABLE 31
HEATS OF FORMATION OF COMPOUNDS

Substance	From the Elements in the Standard State	From the Atoms	Reference
O ₃	-34.5	141.45	(1)
O ₄	0.13	234.79	(1)
OH		102.7	(2)
		104	(17)
		< 116.05	(3)
H ₂ O	57.801	219.251	(1)
H ₂ O ₂	33.59	253.69	(1)
HO ₂		169	(4)
		163.5	(5)
		~ 177	(6)
N ₂ O	-19.65	208.3	(1)
NO	-21.6	121.7	(1)
NO ₂	- 8.03	193.92	(1)
N ₂ O ₄	- 3.06	400.84	(1)
Cl ₂ O	-18.25	97.3	(1)
ClO ₂	-23.5	122.25	(1)
SO	- 6.3	117.6	(1), (13)
SO ₂	70.92	254.12	(1)
SO ₃	93.9	335.75	(1)
ICl		49.41	(7)
IBr	- 9.6	41.4	(1), (8)
BrCl	- 3.07	52.71	(1)
HF	64.0	147.55	(1), (10)
HCl	22.06	101.6	(1), (9)
HBr	8.65	85.80	(1), (11)
HI	- 5.91	69.86	(1), (12)
H ₂ S	5.3	174	(1)
NH		< 102.2	(3)
		~ 90	cf. (15)
NH ₂		~ 132.85	(14)
NH ₃	11.0	249.85	(1)
CH ₄	18.24		(1)
C ₂ H ₄	20.96		(1)
CO	26.84		(1)
CO ₂	94.45		(1)
C ₂ H ₂	-11.0		(1)
C ₂ H ₄	-53.9		(1)
C (atomic)	125.1 (0°K)		(19); cf. (16), (18)

REFERENCES

- (1) Bichowsky and Rossini, *The Thermochemistry of the Chemical Substances*, Reinhold Publishing Corp., New York, 1936.
 (2) Eucken, *Z. Physik*, **29**, 45 (1922).
 (3) Bates, *Z. physik. Chem.*, Bodenstein-Festband, 329 (1931).

- (4) Bray, *J. Am. Chem. Soc.*, **60**, 82 (1937).
- (5) Weiss, *Trans. Faraday Soc.*, **31**, 668 (1935).
- (6) Heitler: see ref. 5, p. 672.
- (7) W. G. Brown and Gibson, *Phys. Rev.*, **40**, 529 (1932).
- (8) Cordes and Sponer, *Z. Physik*, **63**, 334 (1930).
- (9) Beutler and Mee, *Naturwissenschaften*, **22**, 419 (1934).
- (10) Russell, *Astrophys. J.*, **79**, 317 (1934).
- (11) Gordon and Barnes, *J. Chem. Phys.*, **1**, 692 (1933).
- (12) Van Rysselberghe, *J. Phys. Chem.*, **33**, 3371 (1931).
- (13) Martin and Jenkins, *Phys. Rev.*, **39**, 549 (1932).
- (14) Calculated from Ellis, *Phys. Rev.*, **33**, 27 (1929).
- (15) Bonhoeffer and Harteck, *Grundlagen der Photochemie*, Theodor Steinkopf, Dresden, 1933, p. 81.
- (16) Herzberg, Herzfeld, and Teller, *J. Phys. Chem.*, **41**, 325 (1937).
- (17) Haber and Bonhoeffer, *Z. physik. Chem.*, **A127**, 264 (1928); Bonhoeffer and Reichert, *ibid.*, **A129**, 75 (1928); Herzberg, *ibid.*, **B10**, 189 (1930).
- (18) Herzberg, *Chem. Rev.*, **20**, 145 (1937).
- (19) Burton, *J. Chem. Phys.*, **6**, 818 (1938).

TABLE 32

BOND STRENGTHS IN ORGANIC COMPOUNDS

Bond	Strength	Reference
C—C	82.5 (Hydrocarbons)	(7)
	83	(2)
	84.2 (Paraffins)	(3)
	110–115	(5)
	71	(4)
	97.6	(9)
	72 (C ₃ H ₈)	(12)
	89.5 (C ₂ H ₆)	(11)
C=C	162 (C ₂ H ₄)	(11)
	145 (Hydrocarbons)	(7)
	149	(2)
	200	(5)
	125	(4)
	151.2 (Olefins and cyclic compounds)	(3)
C≡C	198.5 (Acetylenic hydrocarbons)	(3)
	220.5 (C ₂ H ₂)	(11)
	200	(2), (7)
	187	(10)
C—H	100 (Hydrocarbons)	(7)
	92.3	(1)
	95 (CH ₄)	(12)
	100 (CH ₄)	(3)
	92	(4)
	114	(5)
	102.5	(8)
	108	(9)
	103 (CH ₄)	(11)
C—O	92	(4)
	82 (Alcohols, ethers)	(7)
	81.8	(2)
	83 (Aliphatic ethers)	(3)
C=O	81 (Aliphatic primary alcohols)	(3)
	178 (HCHO)	(11)
	183.5 (Acetone)	(11)
	188	(4)
	177.8 (Ketones)	(3)
	166.1 (HCHO)	(3)
C—Cl	174.4 (Other aldehydes)	(3)
	78 (Alkyl halides)	(7)
C—Br	73	(4), (6)
	65.3	(2)
C—I	59	(6)
	56.5	(2)
	44	(4), (6)

TABLE 32 (Continued)
BOND STRENGTHS IN ORGANIC COMPOUNDS

Bond	Strength	Reference
C—N	64.2 (CH ₃ NH ₂)	(11)
	66 (Amines)	(7)
	68.4 (Amines)	(3)
C≡N	200 (Nitriles, HCN)	(7)
	202 (HCN)	(3)
	209.2 (Aliphatic cyanides)	(3)
	207.5 (HCN)	(11)

REFERENCES

- (1) Mulliken, *Rev. Mod. Phys.*, **4**, 1 (1932).
- (2) Pauling, *J. Am. Chem. Soc.*, **54**, 3570 (1932).
- (3) Pauling and Sherman, *J. Chem. Phys.*, **1**, 606 (1933).
- (4) Eucken, *Handbuch der Experimental Physik: Energie und Wärmeinhalt*, Akademische Verlagsgesellschaft, Leipzig, 1929, pp. 713–715.
- (5) Mecke, *Nature*, **125**, 526 (1930); *Z. physik. Chem.*, **B17**, 1 (1932).
- (6) Kohlrausch, *Der Smekal-Raman-Effekt*, Julius Springer, Berlin, 1931.
- (7) Rice and Rice, *The Aliphatic Free Radicals*, Johns Hopkins Press, Baltimore, Md., 1935, p. 75.
- (8) Patat, *Z. physik. Chem.*, **B32**, 290 (1936).
- (9) Trenner, Morikawa, and Taylor, *J. Chem. Phys.*, **5**, 203 (1937).
- (10) Price, *Phys. Rev.*, **45**, 843 (1934); *ibid.*, **47**, 444 (1935).
- (11) Norrish, *Trans. Faraday Soc.*, **30**, 103 (1934).
- (12) Burton, *J. Chem. Phys.*, **7**, 1072 (1939).

APPENDIX III

TABLE 33

ACTIVATION ENERGIES OF SOME SIMPLE REACTIONS

(Cf. § 10.5.)

Reaction	Source of Radical or Atom	Activation Energy, kcal.	Reference
$D + NH_3 \rightarrow NH_2D + H$	Hg*	11 ± 1	(1)
$D + CH_4 \rightarrow CH_3D + H$	Hg*	13 ± 1	(1)
$D + H_2O \rightarrow HOD + H$	Hg*	7	(1)
$Hg^* + CH_4 \rightarrow Hg + CH_3 + H$		~ 4.5	(2)
$CH_3 + D \rightarrow CH_2D + H$		≤ 5	(2)
		or $CH_2 + HD$	
$CH_3 + D_2 \rightarrow CH_3D + D$		11	(2) ^a
$CH_4 + D \rightarrow CH_3 + HD$		14	(2)
$CH_3 + CD_4 \rightarrow CH_3D + CD_3$		11–15	(2)
$C_2H_6 + D \rightarrow C_2H_5 + HD$	Hg*	11	(2)
$C_2H_6 + D \rightarrow CH_3D + CH_3$	Hg*	~ 7.5	(2)
$C_2H_6 + Hg^* \rightarrow C_2H_5 + H + Hg$		0	(2)
		or $2CH_3 + Hg$	
		0	(2)
$CH_3 + CH_4 \rightarrow C_2H_6 + H(?)$		~ 16	(2)
$CH_4 + D \rightarrow CH_3 + HD$	Discharge tube.	15.6	(3) ^a
$CH_3 + HD \rightarrow CH_4 + D$		11.1	(3)
$CH_3 + H_2 \rightarrow CH_4 + H$	$(CH_3)_2CO$	11 ± 2	(4)
$CH_3 + H_2 \rightarrow CH_4 + H$	$Na + CH_3Hal$	8, 5.5–6.3	(4), (5)
$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO$		9.8	(6)
$H + HCHO \rightarrow H_2 + HCO$		16.2	(6)

^a Steric factor = 0.1.

REFERENCES

- (1) A. Farkas and Melville, *Proc. Roy. Soc. (London)*, **A157**, 625 (1936).
- (2) Morikawa, Benedict, and Taylor, *J. Chem. Phys.*, **5**, 212 (1937).
- (3) Trenner, Morikawa, and Taylor, *ibid.*, **5**, 203 (1937).
- (4) Taylor and Rosenblum, *ibid.*, **6**, 119 (1938).
- (5) Hartel and Polanyi, *Z. physik. Chem.*, **B11**, 97 (1930).
- (6) Akeroyd and Norrish, *J. Chem. Soc.*, 890 (1936).

APPENDIX IV

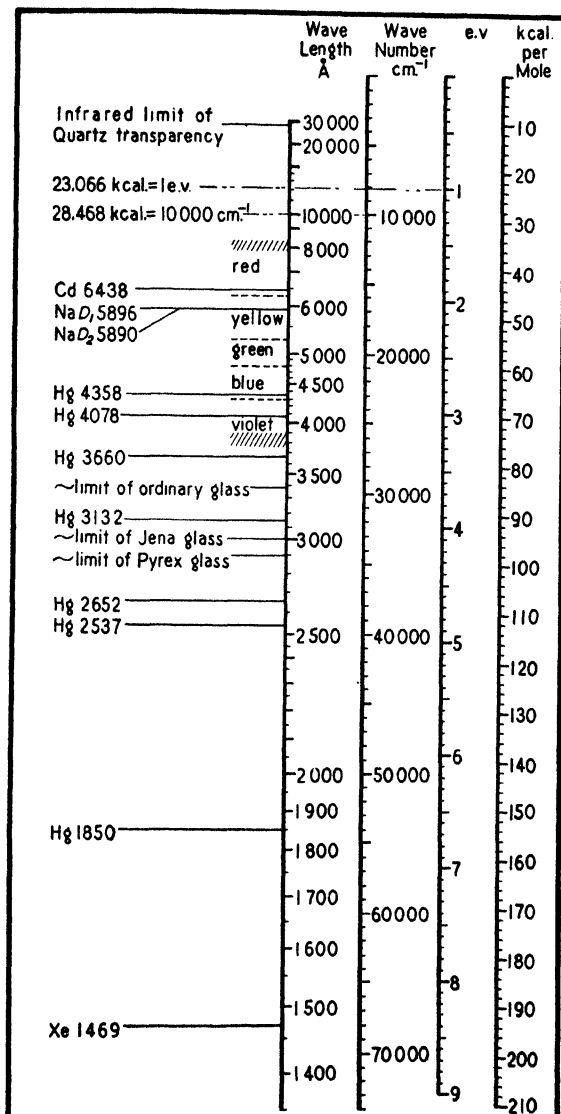


Fig. 59. Energy Conversion Chart.

INDEX

Subject Index

A

Absorption:

by a particular group, 83, 223
curves for:

acetone in hexane, 223
aldehydes in hexane, 222
amyl nitrite, 218
azomethane, 214
bromide ion, 369
chloride ion, 370
diazomethane, 214
ethyl nitrate, 218
ethyl nitrite, 218
fatty acids, 240
hydrogen selenide, 179
hydrogen sulfide, 179
hydrogen telluride, 179
iodide ion, 369
methyl alcohol, 219
methyl cyanide, 221
methyl nitrate, 218
methyl nitrite, 218
nitrate ion, 375
nitric acid in water and ether, 376
nitroethane, 218
nitromethane, 218
ozone in the ultraviolet, 144
ozone in the visible, 143
silver halides, 135
"discoloration" of, 136
water, 172

laws of, 35

Absorption spectra of:

aldehydes, 221
alkali halide crystals, 125
alkyl halides, 203
amines, 212
benzene, 200
ketones, 221

Acetaldehyde:

chain decomposition of, 322
photolysis at high temperatures, 323
photolysis in solution, 359
photo-oxidation of, 325

Acetic acid, photolysis:

gaseous, 242, 363
in solution, 363

Acetone:

absorption, 232
in hexane solution, 223

Acetone (*Cont.*):

fluorescence, 232
photolysis at high temperatures, 323

Acetone sensitized decomposition of
dimethyl ether, 323

Acetyl acetone, polymerization, 239

Acetyl bromide, 245

Acetylchloroaminobenzene, rear-
rangement, 260

Acetyl chloride, 245

Acetylene:

absorption spectrum, 347
addition of chlorine and bromine,
336

formation by photolysis of ethyl-
ene, 342

polymerization, 350

by α , β , and γ rays, 351

by methyl radicals, 350

mercury sensitized, 351

potential energy curves for $C\equiv C$,
349

Acetylene derivatives, polymerization
(table), 347

Acetylene dibromide, addition of
 Br_2 , 336

Acetylene dichloride, addition of
bromine, 334

Acetyl halides:

absorption coefficients, 244
photolyses, 245

Acetyl iodide, 245

Acids, fatty, 239

absorption coefficients, 240

Acids, monobasic, products of pho-
tolysis, 241

Activation energies, 93, 283

calculation of, 95

table, 424

Acyl peroxides, 245

Addition of thermal and photo-
chemical rates, 301

Addition reactions, 325

Alcohols:

absorption curve for methyl, 219
photolyses of, 218

in aqueous solution, 220

Aldehydes:

absorption spectra, 221

in hexane solution, 222

of vapor, 224

Aldehydes (*Cont.*):

- aliphatic, 225
- decomposition:
 - catalyzed by free radicals, 228
 - in aqueous solution, 226
 - in solution, 357
 - into free radicals, 227
 - into ultimate molecules, 229
- polymerization of, 342, 354
- quantum yield of photolysis at different temperatures, 228
- unsaturated aliphatic, 231

Alkali halides:

- absorption spectra of crystals, 125
- model for photochemistry of crystals, 122
- positions of absorption maxima of solid, 127
- solutions, 372

Alkenes:

- absorption spectra, 199
- formed in photolysis of aldehydes, 230

Alkyl cyanides, 221

Alkyl halides, 201

- absorption spectra, 203, 204
- primary reactions in photolysis of, 206

Alkyl iodides, photolysis:

- in presence of silver, 211
- in solution, 361
- quantum yields, 365

Alkyl nitrites, 216

Allocynamidenacetic acid, iodine sensitized rearrangement, 294

Amines:

- absorption of, 212
- photochemistry, 212

Ammonia:

- decomposition, 363
- hydrazine formed in, 183
- mechanism, 183
- mercury sensitized, 282
- quantum yields, 182
- formation, mercury sensitized, 280

Anthracene, polymerization, 352

Atomic spectra:

- correlation of *J* and *L*, 12
- metastable states, 14
- multiplicity, 13
- notation for energy levels, 13
- quantum numbers, 8
- selection rule for:

J, 14*L*, 12*M*, 16

multiplicity, 14

table of *J* values, 13

Zeeman effect, 17

Atoms, detection of, 115

 α -Azidopropiondimethylamide, separation into isomers, 384

Azomethane:

- absorption curve, 214
- photolysis, 215

B

Beer's law, 35, 89

Benzaldehyde:

- conversion to benzoin, 231
- photolysis, 231
- photo-oxidation, 326

Benzene:

- absorption spectrum, 200
- bromination, 357
- chlorination, 338

Bichromates, 376

Blackman reaction, 405

Bohr frequency principle, 3

Bohr's fundamental postulates, 7

Bond strengths, 418, 422, 423

Bromide ion, absorption curve in aqueous solution, 369

Bromine:

addition to:

- acetylene, 336
- acetylene dibromide, 336
- acetylene dichloride, 334
- cinnamic acid, 335
- fumaric ester, 289
- maleric ester, 289
- tetrachloroethylene, 331
- dissociation by light in the band region, 301

reaction with:

- benzene, 357
- hydrogen, 296
- effect of pressure, 297, 299
- oxalate, 382
- platinum, 301

Bromine atoms:

- heterogeneous recombination, 300
- homogeneous recombination, 104

Bromine monoxide, 171

Bromine sensitized:

- decomposition of $C_2Cl_4Br_2$, 330
- oxidation of CCl_3Br , 292
- ozone decomposition, 288
- reactions of maleic acid and its esters (table), 290
- rearrangement of maleic acid, 289
- mechanism, 291

Bromoacetic acid hydrolysis, 361

Bromotrichloromethane:

- oxidation, 292
- reaction with chlorine, 321

Budde effect, 111

Butane, 198

Butyl bromide, conversion of iso to tertiary, 207

Butylene iodide, 211

C

- Cadmium sensitized reaction of ethylene and hydrogen, 346
- Calculation of activation energy, 95
- Carbon dioxide:
 - chlorine sensitized formation, 314
 - phosgene sensitized formation, 315
 - reaction with hydrogen, 280
- Cations in solution, 377
- Chain reactions, 92, 296
 - definition, 296
- Chloride ion, absorption curve in aqueous solution, 370
- Chlorine:
 - addition to:
 - acetylene, 336
 - acetylene dichloride, 333
 - dichloroethylene, 333
 - tetrachloroethylene, 330, 363
 - trichloroethylene, 333
 - reaction with:
 - benzene, 338
 - bromotrichloromethane, 321
 - carbon monoxide (*see also* Phosgene), 313
 - chloroform, 320
 - dichlorobenzene, 340
 - ethylene, 329
 - formaldehyde, 320
 - formic acid, 321
 - hydrogen (*see also* Hydrogen chloride), 303
 - methane, 319
- Chlorine atom, reaction with O_2 , 309
- Chlorine dioxide:
 - decomposition:
 - gaseous, 168
 - in solution, 362
 - sensitized, 292
 - formation, in decomposition of Cl_2O , 292
- Chlorine heptoxide, 170
 - formed in chlorine sensitized decomposition of ozone, 286
- Chlorine hexoxide, 170
- Chlorine monoxide, photolysis:
 - chlorine sensitized, 292
 - in gaseous state, 167
 - in solution, 362
- Chlorine sensitized:
 - decomposition of:
 - chlorine monoxide, 292
 - ozone, 286
 - formation of:
 - carbon dioxide, 314
 - water, 308
 - oxidation of:
 - chloroform, 363
 - tetrachloroethylene, 363
 - trichloroethylene, 333

- Chlorine trioxide, 170
 - formation in sensitized decomposition of ClO_2 , 293
 - formed in Cl_2 sensitized decomposition of O_3 , 286
 - thermal reaction with ozone, 286
- Chloroform:
 - chlorine sensitized oxidation, 320, 363
 - reaction with chlorine, 320
- Chlorophyll:
 - absorption spectrum, 399
 - fluorescence, 402, 405, 407
 - in ether, 400
 - formula, 398
 - photo-oxidation, 380
- Cinnamic acid:
 - addition of bromine and chlorine, 335
 - cis-trans* isomerization, 259
- Citraconic acid, isomerization, 259
- Cl_3 :
 - in chlorination of C_2Cl_4 , 330
 - in hydrogen chloride synthesis, 306
 - in phosgene synthesis, 317
- Collision of second kind, 37
- Combination principle, 9
- Complete chemical equilibrium, law of, 112
- Conversion chart for energies, ν , and λ , 425
- Conversion of excitation energy into kinetic energy, 48
- Correlation of absorption coefficient and transition probability, 38
- Cycloketones, 238

D

- Detailed balancing, law of, 112
- Deutero-ammonia:
 - induced predissociation in, 185
 - photolysis:
 - mechanism, 187
 - mercury sensitized, 283
 - quantum yields, 186
- Deviations from Beer's and Lambert's laws, 36
- Diacetyl:
 - fluorescence of, 233
 - formation in photolysis of acetone, 236
- Diazomethane:
 - absorption curve, 214
 - photolysis, 213
- Diborane, 195
- Dibromethylene, *cis-trans* photostationary state, 259
- Dibromotetrachloroethylene, Br_2 sensitized decomposition, 332

- Dichlorobenzenes, reaction with chlorine, 340
 Dichloroethylene, *cis-trans* photostationary state, 259
 Dimethyl ether decomposition photosensitized by acetone, 323
 Di-*n*-propyl ketone, 359
 Diphenyl absorption spectrum, 200
 Disproportionation of:
 ethyl radicals, 210
 radicals, 364
 Dissociation of molecules by light, 60
 Distribution of molecules among energy states, 34
 Draper effect, 111

E

- Eder reaction, 381
 Electronic bands:
 Fortrat diagram, 22
 frequencies of *P*, *Q*, *R* branches, 21
 vibrational structure, 28
 Electron spin, 12
 Energy conversion chart, 425
 Energy deficiency, supplied from several degrees of freedom, 408
 Energy level diagram for:
 mercury, 15
 sodium, 11
 Energy levels, 8
 Esters, 244
 Ethane, photolysis, 198
 Ethyl diazoacetate, photolysis in solution, 366
 Ethylene:
 polymerization of, 342
 by ethyl radicals, 344
 by methyl radicals, 344
 reaction with:
 chlorine, 329
 hydrogen, 344
 cadmium sensitized, 346
 iodine, 294
 Ethylene derivatives, polymerization (table), 347
 Ethylene iodide:
 iodine sensitized decomposition, 293
 photolysis, 211
 Ethyl iodide, quantum yields in photolysis, 208
 Ethyl ketone, photolysis in liquid paraffin, 358
 Ethyl nitrite, as detector of free radicals, 118
 Excitation in carbonyl group, 223
 Extinction (*see* Absorption)

F

- F* centers, 121
 production of, 129
 quantum yields in, 130
 relation to photography, 389

- F'* centers, 124
 production of, 132
 First law of photochemistry, 1
 Fluorescence, 40
 chlorophyll, 400, 405
 definition, 37, 40
 equation for quenching in, 42
 gases, 55
 iodine vapor, 49
 leaves, 412
 liquids, 56
 mercury, 44
 selenium, 54
 sodium, 42
 sodium iodide, 65
 solutions, 57
 sulfur, 54
 tellurium, 54
 Fluorine oxides, 166, 167
 Formaldehyde:
 mercury sensitized formation from CO and H₂, 279
 oxidation of, 323
 photolysis at high temperatures, 323
 predissociation in, 83
 reaction with chlorine, 320
 Formic acid:
 photolysis, 241
 reaction with chlorine, 321
 Formyl chloride, 321
 Fortrat diagrams, 22
 Franck-Rabinowitch hypothesis, 355
 Free radicals:
 catalysis of aldehyde decompositions, 228
 detection of, 115
 disproportionation, 210, 364
 Fumaric acid, rearrangement to maleic, 258

G

- g* terms in molecular spectra, 24
 Germane, 194
 Glyoxal, Hg sensitized formation from CO and H₂, 279

H

- Halides:
 alkali, 125
 alkyl, 201
 in solution, 368
 methyl, absorption coefficients, 203
 Halogen atoms, recombination, 103
 heterogeneous, 105
 homogeneous, 104
 Halogens:
 addition reactions of, 329
 to cyclic compounds, 338
 as sensitizers, 285

Heats of activation, 94, 283
 calculation, 95
 table, 424
Heats of dissociation:
 from spectra, 67
 of halogens, 64
Heats of reaction, 418-421
Herschel effect, 389
HO₂, formation from H and O₂, 276
Hydrazine:
 occurrence in the photolysis of ammonia, 183
 photolysis, 184
Hydrogen:
 atoms:
 reactions with:
 carbon monoxide, 109
 ethylene, 345
 halogens, 109
 hydrocarbons, 109
 hydrogen, 108
 hydrogen halides, 109
 oxygen, 109, 275, 309
 dissociation by:
 mercury, 45, 268
 xenon, 267
 ortho and para, 27
 reaction with:
 carbon dioxide, 280
 carbon monoxide, 279
 nitrous oxide, 280
 oxygen, 272
 mercury sensitized, 274
Hydrogen bromide:
 photolysis, 193
 photosynthesis, 296
 effect of pressure, 297, 299
 mechanism, 297
 rate of thermal formation, 297
Hydrogen chloride:
 absorption, 189
 formation in mixtures of ICl, Cl₂, and H₂, 312
 photosynthesis:
 effect of:
 impurities, 307
 moisture, 308
 oxygen, 308
 temperature, 305, 310
 wave length, 310
 induction period, 307
 in pure hydrogen and chlorine, 303
 mechanism, 304
 with light in Cl₂ band region, 311
Hydrogen iodide:
 photolysis:
 gaseous, 190
 in solution, 370
 photo-oxidation, 276

Hydrogen peroxide:
 absorption, 175
 decomposition:
 gaseous, 176
 in solution, 379
 formation:
 by atomic hydrogen in H₂-O₂ mixtures, 275
 in hydrogen-oxygen mixtures, 272
 mercury sensitized, 275
 in photolysis of water vapor, 173
Hydrogen selenide:
 extinction coefficients for, 179
 photolysis, 180
Hydrogen sulfide:
 extinction coefficients for, 179
 photolysis of, 178, 363
Hydrogen telluride, extinction coefficients for, 179
Hydrolysis of:
 bromoacetic acid, 361
 monochloroacetic acid, 360
Hydroxides in solution, 373

I

Induced predissociation, 74
 in aldehydes, 230
 in deuteroammonia, 185
 in iodine, 52
Iodide ion, absorption curve in aqueous solution, 369
Iodides, alkyl, 361
Iodine:
 addition to:
 β -amylene, 335
 butene, 335
 dicyclopentadiene, 335
 ethylene, 294
 phenyl acetylene, 335
 induced predissociation, 52
 reaction with oxalate, 382
Iodine sensitized:
 decomposition of ethylene iodide, 293
 rearrangement of allocynamyliden-acetic acid, 294
Iron carbonyl, decomposition, 362
Isomerization, 248
 cis-trans effect of pressure, 254
 cis-trans effect of temperature, 253
 cis-trans effect of wave-length, 255
 cis-trans experimental data, 257
 cis-trans model for, 249
 cis-trans potential energy curves, 251, 255, 257
 of nitrobenzaldehydes, 262
Isopropyl radicals, rearrangement to propyl, 264

K

- Ketene, photolysis of, 239
- Ketones, 221
 - absorption spectra, 232
 - table, 233
- decomposition:
 - in solution, 357
 - yielding alkyl radicals, 235
- photochemistry, 234
- Kinetics of reactions, 89
- Kinetic theory and rates of reaction, 92

L

- Lambert's law, 35, 89
- Latent image, 133, 388
- Law:
 - absorption, 35
 - Beer's, 35, 89
 - first, of photochemistry, 1
 - microscopic reversibility, 112
 - photochemical equivalence, 2
- Lead tetraethyl, 362
- Lead tetramethyl, 247
- Life period of activated molecules,
 - 37, 78
 - in solution, 56
 - measurement of, 39
- Light absorption:
 - in terms of potential energy curves, 62
 - proportional to concentration, 89
- Line spectra (*see also* Atomic spectra), 8
- Lithopone, as a sensitizer, 386

M

- Magnetic splitting of the *D* lines, 17
- Maleic acid, bromine sensitized rearrangement, 289
- Maleic ester, reactions with bromine, 289
- Mean free path, 93
- Mechanism:
 - calculation of rate law from, 304
 - for a reaction (general), 101
 - selection of a, 113
- Mercury:
 - energy level diagram, 15
 - fluorescence, quenching, 44
 - by hydrogen, in the presence of nitrogen at 750° C., 270
 - by nitrogen at 750° C., 270
 - by oxygen, 47, 274
 - to 6°P., 268
 - by various gases, 49
- Mercury dimethyl, photolysis, 247
- Mercury hydride, 46
- Mercury sensitized:
 - decomposition of:
 - ammonia, 282
 - nitrous oxide, 152

- Mercury sensitized (*Cont.*):
 - dissociation of hydrogen, 268
 - formation of ammonia, 280
 - polymerization of acetylene, 351
 - reactions, 268
 - of hydrogen with:
 - ethylene, 344
 - nitrous oxide, 280
- Metallo-organic compounds:
 - photochemistry, 247
 - table, 246
- Methane:
 - chlorination, 319
 - photolysis, 196
- Methyl alcohol, extinction coefficients for, 219
- Methylantracene, polymerization of, 352
- Methyl bromide, extinction coefficients, 203
- Methyl chloride, extinction coefficients, 203
- Methyl cyanide, extinction coefficients, 221
- Methyl-ethyl ketone:
 - fluorescence, 232
 - photolysis:
 - gaseous, 232
 - in liquid paraffin, 358
- Methyl iodide, extinction coefficients, 203
- Methyl nitrite:
 - absorption curve, 218
 - as detector of free radicals, 118
- Methyl radicals:
 - catalysis of decomposition of:
 - acetaldehyde, 322
 - dimethyl ether, 323
 - polymerization of acetylene by, 350
 - reaction with nitric oxide, 247
- Microscopic reversibility, law of, 112
- Molecular diameters, 93
- Molecularity of reactions, 100
- Molecular spectra, 17
 - multiplicity, 24
 - odd and even terms, 24
 - positive and negative terms, 26
 - quantum numbers, 24-26
 - symmetrical and antisymmetrical terms, 26
- Monochloroacetic acid, hydrolysis, 360
- Morse curves, 32
- Multiplicity and periodic table, 15

N

- Nickel carbonyl, photolysis, 366
- Nitrate ion, absorption coefficients, 375
- Nitrates, photolysis in solution, 375
- Nitric acid, absorption coefficients in water and ether, 376

- Nitric oxide:
 absorption spectrum, 155
 detection of free radicals by, 118
 photolysis of, 155
 potential energy curves, 157
 reaction with methyl radicals, 247
Nitrites, alkyl, 216
Nitrobenzaldehyde, rearrangement of, 261
Nitroethane, 217
Nitrogen dioxide:
 decomposition, 160, 362
 potential energy curves for, 162
 predissociation spectrum, 160
 sensitizer in N_2O_5 decomposition, 284
Nitrogen pentoxide:
 absorption spectrum, 164
 photolysis, 165, 362
 sensitized by NO_2 , 284
 NO_3 , absorption spectrum, 165
Nitromethane, 217
Nitrosyl chloride, 165
Nitrous oxide, photolysis, 152
Notations for atomic energy states, 13, 417

O

- Olson's model for *cis-trans* rearrangements, 249
Optical isomers, photochemical separation, 384
Order of reaction, 100
Ortho- and para-hydrogen, 27
Oxalates, reactions with:
 bromine, 382
 iodine, 382
 mercuric chloride, 381
Oxalic acid, photolysis, 243
 uranyl sensitized, 381
Oxygen, reaction with hydrogen, 272
Ozone:
 absorption coefficients:
 in the ultraviolet, 144
 in the visible, 143
 formation, 327
 in reaction of H_2O_2 mixtures, 272
 mercury sensitized, 283
 photolysis, 145
 bromine sensitized, 288
 chlorine sensitized, 286
 reaction with chlorine trioxide, 286

P

- Para-ortho hydrogen conversion, used in detection of atoms and radicals, 116
Permanganates, 376
Phenyl chloride, reaction with chlorine, 339

- Phosgene:
 formation of, 313
 oxidation of, 315
Phosgene sensitized formation of carbon dioxide, 315
Phosphine, 188
Phosphorus, polymerization, 353
Photochemical equivalence law, 2, 90
Photochemical rates, addition to thermal, 301
Photochemical threshold, 266
Photodissociation, 60
 of alkali halide vapors, 64
 table of processes and effective wave lengths, 87
Photoelectric effect, 7
Photography, 388
 effect of conditions of precipitation of halide, 394
 quantum yield of elementary process, 390
 table, 392
 sensitivity of grain, 391
 sensitivity specks, 393
 sensitization by dyes, 395
Photolysis of:
 inorganic vapors, 142-195
 organic vapors, 196-247
 solids, 121-141
Photo-oxidation of chlorophyll, 380
Photoreduction of thionene dyes, 380
Photosensitization, 266
 definition, 266
 in solution, 378
Photostationary state in isomerizations, 258-259
Photosynthesis, 396
 Blackman reaction, 405
 in vitro, 413
 locus of, 401
 mechanism, 408
 oxygen-carbon dioxide ratio in, 400
 photosynthetic unit, 406
 products, 400
 quantum yields:
 with chlorella, 403
 with purple bacteria, 404
 studies with radio-carbon, 413
 threshold of activity, 397
Polarized light, effect of:
 circularly, 383
 on solids, 141
Polymerization, 341
 definition, 341
Potential energy curves, 30
 acetylene, 349
 cis-trans isomerizations, 252, 255, 257
 ethylene, 250
 halogens, 61
 iodine, 82

Potential energy curves (*Cont.*):
 light absorption referred to, 62
 nitric oxide, 157
 nitrogen dioxide, 162
 predissociation, 72
 RHC=CHR , 251
 sulfur, 31
 Predissociation, 69
 definition, 70
 effect of temperature, 77
 heats of dissociation from, 76
 induced, 52, 74, 185, 230
 mechanism, 71
 of formaldehyde, 83
 of iodine, 81
 of nitrogen dioxide, 160
 of polyatomic molecules, 74
 of sulfur, 78
 of sulfur dioxide, 85
 potential energy curves, 72
 selection rules, 73
 tests, 77
 Propane, 198
 Propionic acid, 243
 Propyl bromide, conversion of *n* to
 iso, 207

Q

Quanta, 2, 4
 Quantum numbers for:
 atomic spectra, 8
 molecular spectra, 25
 Quantum yield:
 comparison of, in gas and solution,
 362
 definition, 3, 90
 dependence on:
 light intensity, 113
 temperature, 228
 wave length, 289, 294, 311, 336,
 366
 in condensed systems, 366
 in solution, 362, 365
 of elementary photographic proc-
 ess, 390
 of isomerizations, 259, 262
 of photolysis:
 alkyl iodides, 145
 ammonia, 182
 deuteroammonia, 186
 hydrogen iodide in water and
 hexane, 371
 nitrogen dioxide, 162
 ozone, 145
 silver halides, 137
 of production of *F* centers, 130
 Quartz, extinction coefficient of, 172
 Quenching of fluorescence in:
 mercury vapor, 44
 sodium vapor, 43
 solutions, 57

R

Radicals:
 disproportionation reactions of,
 107, 364
 recombination, 105
 Radio-carbon, used in photo-
 synthesis, 413
 Rate constants, values for steps in
 mechanism for formation of
 HBr , 300
 Rate law:
 calculation from mechanism, 298,
 304
 determination of, 98
 Rates:
 addition of thermal and photo-
 chemical rates, 301
 kinetic theory of, 92
 Reaction kinetics, 89
 Reaction mechanisms, steps in, 114
 Reactions of alkyl radicals, 110
 of HCO , 229
 Rearrangements, 248
 of acetylchloroaminobenzene, 260
 of benzoylchloroaminobenzene, 260
 of *cis-trans*, 253
 of isopropyl radicals, 264
 of *o*-nitrobenzaldehyde, 261
 of *trans* to *cis* stilbene, 258
 stationary state in, 258
 Recombination of:
 bromine atoms, 104, 300
 halogen atoms, 103
 hydrogen atoms, 102
 radicals, 105
 Resonance, 41
 of sodium vapor, 42
 Rotation about a double bond, 248
 Rotation spectra, equation for ob-
 served frequencies, 18
 Rydberg constant, 10
 Rydberg series, 10

S

Selection rules for:
 atomic spectra, 12, 14
 molecular spectra, 24-26
 predissociation, 73
 Selenium, fluorescence, 54
 Sensitization:
 by dyes in photography, 395
 by halogens, 285
 by uranyl ion, 381
 Sensitized decompositions (table), 285
 Sensitized fluorescence of TI vapor,
 268
 Sensitized reactions, 266
 Sensitizers, white pigments as, 385
 Silanes, 194

Silver halides:
 absorption curves for, 135
 discoloration, 136
 in photography, 388
 photochemistry, 133
 quantum yields of photolysis, 137
 Sodium:
 energy level diagram, 11
 resonance of vapor, 42
 Sodium hydroxide absorption coefficient in solution, 373
 Solids, table of photochemical studies, 140
 Solvent effects, specific, 366
 Specific reaction rate, 94
 Spectra:
 atomic, 8
 molecular, 17
 Spectroscopic heats of dissociation of the halogens, 64
 Stilbene, *cis-trans* rearrangement, 258
 Stokes' rule for fluorescence, 51
 Succinic acid, photolysis, 243
 Sulfite solutions, photolysis, 374
 Sulfur:
 change from S_λ to S_μ , 354
 compounds in solution, 373
 fluorescence, 54
 potential energy curves, 31
 predissociation, 78
 Sulfur dioxide:
 absorption spectrum, 147
 photolysis, 147
 predissociation, 85
 Sulfur trioxide, photolysis, 151

T

Tellurium, fluorescence, 54
 Term values, definition, 10
 Tetrachloroethylene:
 addition of:
 bromine, 330
 chlorine, 330, 363
 chlorine sensitized oxidation, 331, 363
 Thallium sensitized fluorescence, 268
 Thermal rates, addition to photochemical, 301

Thionene dyes, photoreduction of, 380
 Time between collisions, 93
 Titanium dioxide, as a sensitizer, 386
 Transference between vibrational states, 52
 Transfer of Hg from 6^3P_1 to 6^3P_0 state, 48
 Transition probability, estimation from absorption coefficient, 38
 Trichloroethylene:
 addition of chlorine, 333
 Cl_2 sensitized oxidation, 333

U

U bands, 131
u terms in molecular spectra, 24
 Uncertainty principle, 33, 70, 71
 Uranyl ion:
 reduction by oxalate, 382
 sensitizer for oxalate decomposition, 381

V

Vibration-rotation spectra, 19
 definition of *P* and *R* branches, 20
 Vinyl iodide, photolysis, 206

W

Water:
 absorption curve for vapor, 172
 chlorine sensitized formation, 308
 mercury sensitized:
 decomposition, 284
 formation, 274
 photolysis, 172
 White pigments, absorption limits of, 387

X

Xenon sensitized dissociation of H_2 , 46, 267

Z

Zeeman effect, 17
 Zinc oxide, as a sensitizer, 385

Author Index

A

Aickin, 312
 Akeroyd, 227, 228, 323, 424
 Albu, 373
 Allen, 106, 119, 228
 Allmand, 176, 243, 286, 303, 305, 308,
 310, 379, 382
 Almasy, 231
 Alyea, 347, 379
 Amdur, 102
 Anderson, 217, 379
 Angenot, 212
 Appleyard, 108, 233, 237
 Arends, 223, 232, 239, 240, 244
 Armstrong, 347
 Arnold, 406, 407
 Ashdown, 347
 Ashley, 313
 Asundi, 147, 246
 Avery, 180

B

Bach, 140
 Bäckström, 231, 326
 Badger, 301
 Bailey, 379
 Ballard, 419
 Baly, 354, 375, 413
 Bamford, 230, 238, 358
 Bandel, 134
 Banov, 212
 Barak, 236, 278
 Barker, 354
 Barnes, 261, 419, 421
 Bates, 111, 183, 201, 210, 271, 275,
 276, 282, 285, 320, 344, 346, 350,
 420
 Bauer, 335
 Baur, 378, 385
 Bawn, 106
 Baxter, 162, 164
 Bayliss, 311, 312
 Beatty, 326
 Beckman, 183, 184, 285
 Bellenot, 382
 Benedict, 110, 185, 285, 424
 Beretta, 146
 Bergstrom, 182, 185, 363
 Bernreuther, 308
 Berry, 42
 Berthelot, 189, 223, 341, 350
 Berthoud, 289, 336, 382

Bethe, 128
 Beutler, 46, 49, 269, 281, 282, 419, 421
 Bhattacharyya, 334, 335
 Bichowsky, 165, 420
 Birge, 67, 272, 419
 Blacet, 224, 227, 229, 354
 Blackman, 405
 Blair, 322
 Block, 233, 238, 396
 Blum, 195
 Bodenstein, 3, 91, 104, 105, 109, 117,
 167, 169, 190, 193, 276, 286, 292,
 290, 297, 299, 302, 303, 305, 308,
 313, 314, 316, 319, 326
 Boeseken, 246
 Böhm, 275, 305
 Bohr, 7
 Boissanas, 377
 Bokorny, 397
 Bolland, 188
 Bonhoeffer, 4, 64, 71, 91, 109, 140,
 174, 177, 191, 273, 275, 276, 286,
 290, 305, 313, 327, 352, 421
 Booher, 87, 192, 336
 Booth, 169
 Borinski, 289
 Born, 126
 Bowen, 169, 233, 262, 288, 326, 358,
 362
 Bradshaw, 178, 363
 Bray, 177, 276, 421
 Brenschede, 171, 319
 Briers, 382
 Brings, 183
 Brodersen, 167
 Brodinan, 262
 Brosset, 140
 Brown, W. G., 421
 Bruner, 289
 Brunner, 401
 Bunsen, 308
 Burgess, 307
 Burk, 341
 Burns, G. R., 398
 Burton, 70, 107, 120, 187, 216, 225,
 227, 228, 235, 236, 241, 242, 243,
 349, 421, 423
 Buston, 401
 Butkow, 372
 Byk, 352
 Byrns, 169, 286

C

Calvert, 46, 267
 Cameron, 141
 Campbell, 110, 174, 271
 Cantieni, 220
 Cario, 4, 45, 268, 269
 Carr, 199, 200, 201
 Carrico, 331, 332, 363
 Carroll, 396
 Carruthers, 323, 326
 Carwile, 160
 Chapman, A. T., 363
 Chapman, D. L., 307, 313
 Chattaway, 261
 Cheung, 362
 Childs, 39
 Christensen, 42
 Christiansen, 297
 Christy, 78, 419
 Chuard, 401
 Ciamician, 261
 Clayton, 156
 Clemo, 404
 Cline, 178, 363
 Coehn, 87, 173, 189, 308, 319
 Cohn, 262
 Colange, 143
 Conrad-Billroth, 222
 Cook, 271
 Copaux, 271
 Coper, 384
 Corbiere, 160
 Cordes, 149, 319, 421
 Craggs, 303, 305, 308, 310
 Cramer, 344
 Cremer, 309
 Crist, 367, 373
 Crumpler, 217
 Cultrera, 375
 Curtis, H., 379

D

Dain, 177, 361
 Dainton, 216
 Dam, 379
 Damon, 237
 Daniels, 160, 162, 164, 237, 284, 331,
 335, 362, 403
 Das Gupta, 294
 Datta, 93, 192
 Davis, 107, 216, 236
 Dawsey, 163, 164, 175
 deBoer, 123
 de Hemptinne, 231
 DeRight, 211, 294, 334
 Desai, 419
 Deutschbein, 377
 Dhar, N. R., 354, 373, 414
 Dickinson, 162, 164, 274, 282, 294,
 330, 331, 332, 360, 361, 362, 363,
 386

Dieke, 84, 224, 267
 Dieterle, 392
 Dixon, 166, 181, 184
 Doctor, 181
 Dorgelo, 40
 Dubrisay, 206
 Duggar, 403
 Duncan, 152, 185, 196, 233
 Dunoyer, 41
 Dutheil, 144
 Dutta, 147, 164
 Dux, 308
 Dyduszyński, 197
 Dymond, 60

E

Eastwood, 222
 Ecker, 396
 Eggert, 289, 391, 392
 Eibner, 385
 Einstein, 2, 7, 60
 Eisenbrand, 375, 376
 Elbs, 373
 Eliashevich, 52
 Elliott, 166
 Ellis, 421
 Ells, 233
 Emeleus, 194, 212, 342, 344
 Emerson, 406
 Emschwiller, 107, 206, 364
 Englemann, 402
 Etzler, 244
 Eucken, 328, 420, 423
 Evans, 274
 Ewart, 402
 Eyber, 363
 Eyring, 96, 306

F

Fajans, 151, 394
 Farkas, A., 28, 108, 116, 117, 424
 Farkas, L., 64, 71, 102, 117, 183, 191,
 220, 226, 229, 241, 276, 285, 353,
 360, 363, 378
 Farquharson, 170
 Farrer, 139
 Fazel, 284
 Feldmann, 391, 392
 Fergusson, 176
 Fesefeldt, 140
 Fichter, 247
 Fielding, 224, 354
 Finkelnburg, 167, 168, 205, 362
 Fischer, 398, 404
 Fisk, 234, 340
 Fiske, 233
 Fletcher, 115, 219
 Flory, 154
 Fonzes-Diaczon, 181
 Forbes, 146, 178, 180, 211, 215, 335,
 363, 377, 381

Forerand, 181
 Förster, 212
 Forster, 238
 Fowler, R. H., 39
 Franck, 4, 45, 46, 48, 51, 57, 60, 65,
 86, 87, 88, 149, 268, 269, 313, 356,
 369, 370, 402, 405, 408
 Frank, I. M., 274
 Franke, 337
 Frankenburger, 109, 229, 276, 278,
 279, 394
 Franz, 84, 224, 229
 Frenkel, 387
 Fricke, 378
 Friedländer, 262
 Frisch, 167
 Froentjes, 265
 Fromherz, 369
 Fues, 126
 Fuller, 81

G

Garbatski, 117
 Gardner, 386
 Garratt, 246, 363, 366
 Gaudechon, 189, 223, 341, 350
 Gaviola, 46, 56, 269, 281
 Gedye, 183
 Gee, 313
 Geib, 108, 109, 116, 118, 174, 183,
 279
 Gelissen, 246
 Gerke, 191
 Germer, 64
 Ghosh, 294, 334, 335
 Giauque, 156, 419, 423
 Gibson, G. E., 419, 421
 Gibson, K. E., 364, 365
 Gillette, 240
 Ginsberg, 208, 365
 Glasbrook, 215
 Glazebrook, 208, 235, 236, 238, 264
 Glissman, 166
 Gloor, 140
 Gogoberidze, 123
 Goldfinger, 373
 Goldstein, 133
 Goodeve, C. F., 151, 167, 170, 173,
 178, 180, 202, 203, 205, 362, 385,
 388
 Goodeve, J. W., 216
 Gordon, A. R., 421
 Gordon, N. E., 382
 Gorin, 240, 241
 Gorup-Besanez, 401
 Gradstein, 84, 224
 Graffunder, 40
 Grauath, 171
 Grant, 387
 Gray, S. C., 353
 Grieneisen, 198, 342

Griffith, 382
 Griffiths, 271
 Grote, 173
 Groth, 183, 196
 Grüss, 292, 322
 Gudden, 132
 Guerlain, 223
 Guha, 140
 Gurney, 123, 389
 Gyulai, 132

H

Haber, 177, 276, 370, 374, 421
 Halford, 261
 Hamann, 170
 Hamer, F. M., 396
 Hammick, 217
 Hamos, 43
 Hankin, 349
 Hantzsch, 369
 Hantzsch, 239
 Harris, 160, 347
 Harrold, 213
 Hart, 338, 339, 378
 Hartock, 108, 109, 116, 117, 118, 169,
 177, 183, 273, 276, 279, 286, 290,
 327, 352, 421
 Hartel, 424
 Hartley, 262
 Hartung, 391
 Hasenkamp, 404
 Hassid, 413
 Hay, 389
 Hecht, 137, 392
 Heidt, 91, 144, 146, 215, 377, 379
 Heil, 54
 Heilbron, 354
 Heinrich, 194
 Heitler, 27, 419, 421
 Helbig, 132
 Hempbel, 181
 Hemphill, 213
 Henkin, 243
 Henri, 69, 77, 78, 84, 147, 160, 176,
 200, 212, 223, 224, 239, 379
 Henrici, 205
 Henry, 152
 Hermans, 246
 Herold, 222, 223, 232
 Hertel, 305, 310
 Herzberg, 30, 47, 71, 78, 84, 156, 161,
 175, 180, 195, 203, 205, 212, 218,
 221, 224, 229, 272, 328, 348, 419, 421
 Herzfeld, 88, 119, 228, 297, 402, 408,
 419, 421
 Heyde, 319
 Hibben, 140
 Hilferding, 104, 297
 Hilgendorff, 181, 342
 Hill, 211
 Hillmer, 201

Hilsch, 124, 129, 132, 135, 136, 137,
140, 392
Hinshelwood, 118, 271, 288
Hirschlaff, 216
Hirshberg, 220, 226
Hocart, 271
Hoch, 219
Hoffman, 140
Hogness, 65
Holmes, 162, 164, 284, 362
Hoover, 397
Hopfield, 267
Hornel, 261
Howe, 196, 233, 237
Hückel, 249
Hudson, 249
Hukumoto, 202, 205
Hund, 24

I

Imanishis, 184
Ionescu, 265
Iredale, 205, 210, 313, 364, 365

J

Jackson, 177
Jahn, 107, 216, 218, 236
Jeffreys, 362
Jelley, 396
Jenkins, 148, 421
Jette, 57
Jeu, 347, 379
Johnston, E. H., 284
Johnston, H., 168
Johnston, H. L., 154, 419
Jolley, 212
Jones, E. J., 164
Jones, F. W., 312
Jones, L. T., 210, 320
Jones, W. H., 344
Jorissen, 327
Joseph, 49
Jost, 104, 297
Juday, 403
Jung, 104, 109, 297, 299, 308
Jungers, 184, 212, 283, 344, 346

K

Kailan, 258
Kamen, 413
Kandler, 396
Kaplan, 45, 157
Karrer, 284
Kassel, 88, 92, 271
Kautski, 408
Kay, 402
Keidel, 386
Kellerman, 307
Kelley, 419
Kempff, 262
Kemula, 196, 197, 351

Kernbaum, 173
Kieser, 392
Kimball, 276
Kirkbride, 84, 213, 227, 235
Kistiakowsky, 59, 84, 145, 165, 167,
177, 183, 200, 224, 239, 248, 271,
292, 347
Kitchener, 388
Klemenc, 345
Klemm, 126
Klingelhoefer, 110, 304
Klinkhardt, 229, 276, 278
Knauss, 157, 419
Knopf, 384
Koch, 391
Koehler, 53
Koenig, 183
Kohlrausch, 202, 423
Kolsch, 212
Kondratjew, 65, 79, 81, 103, 144, 145,
301
Konstantinova-Schlezing, 150
Kopsch, 177, 273
Kornfeld, 149, 151, 176, 276, 379
Kostytschew, 400, 402
Krauskopf, 309, 320
Kreiss, 391
Kreusler, 171
Krishnan, 140
Krolkowski, 289
Kronig, 28, 71, 201
Kruger, 352
Kublitskii, 347
Küchler, 264
Kuhn, H., 65, 87
Kuhn, W., 383, 384
Kummerer, 262

L

Lambrey, 154, 160
Lammert, 367
Landsberg, 181
Lange, 376
Langmuir, 269
Lardy, 233
Läuchle, 143
Laudenklos, 196
Lauer, 352
Lauris, 79
Lavin, 177, 271
Leermakers, 111, 228, 322, 323, 330,
331, 363, 390
Lehman, 104
Leifson, 154, 160, 171, 196
Leighton, P. A., 106, 120, 182, 185,
196, 224, 226, 227, 246, 262, 278,
360, 362, 363
Leighton, W. G., 226, 278, 360, 381
Leipunsky, 103
Lenher, 316
Leonhardt, 123
Lescyuski, 395

Levene, 222
 Levi, 57, 408
 Lewis, B., 177, 191, 271, 280, 288
 Lewis, G. N., 114, 258
 Lewschin, 56
 Ley, 223, 232, 239, 240, 244, 373
 Libby, 356
 Lieneweg, 190
 Lifschitz, 265
 Lind, 297, 347, 350
 Lindquist, 312
 Linnett, 224, 246, 354
 Linstrom, 205
 Lipkin, 258
 Lipp, 348
 Lippman, 401
 Littleton, 123
 Livingston, 347, 350, 351
 Löb, 275
 Lochte-Holtgreven, 30, 43, 78
 Löcker, 84, 227
 Loew, 397
 Löhle, 134
 London, 27, 94
 Long, E. A., 419
 Long, F., 261
 Loomis, 81
 Lotmar, 147
 Lucy, 262
 Ludlam, 342
 Luther, 352, 392
 Lütkemeyer, 104, 296
 Lyman, 171

M

Macdonald, 152
 MacDougall, 240
 MacMahon, 307
 Magel, 258
 Mahneke, 194, 211, 259
 Manning, 233, 237, 403
 Mannkopf, 43
 Maroney, 249
 Marshall, 275, 276, 279, 341
 Martens, 138, 392
 Martin, 148, 421
 Matheson, 233
 Mathews, 379
 Mayneord, 201
 McCaig, 149
 McDonald, 342
 McIlwain, 404
 McKeown, 382
 McMorris, 386
 Mecke, 39, 160, 173, 229, 423
 Mee, 421
 Meissner, 40
 Mellor, 313
 Melville, 184, 188, 281, 347, 350, 353, 424
 Melvin, 144
 Menschick, 369
 Meyer, 45, 269

Meyers, 341, 345
 Millon, 169
 Mills, 205
 Mitchell, 47, 282
 Moelwyn-Hughes, 288
 Mohile, 377
 Mohler, 43
 Molisch, 402
 Mollwo, 131, 132
 Montgomery, 315
 Mooney, 342
 Morey, 243
 Morgan, 367, 373
 Morikawa, 84, 110, 285, 423, 424
 Morse, 32
 Morten, 375
 Mortensen, 106, 120, 246, 362
 Moses, 181
 Mosset, 289
 Mott, 123, 126, 129, 389
 Mudrovic, 375
 Müller, 57, 333
 Mulliken, 28, 82, 156, 158, 195, 256, 423
 Mund, 184, 351
 Mundie, 30, 78
 Murthi, 294
 Mutter, 392
 Myers, 285
 Mzrazek, 351

N

Nagai, 362
 Narayanswamy, 140, 141
 Naude, 78, 419
 Negelein, 363, 403, 405
 Neher, 373
 Neiger, 377
 Nelson, 211, 335
 Nernst, 60, 304
 Neujmin, 87, 172, 181, 220, 273
 Neumann, 336
 Neuschul, 377
 Neuweiler, 385
 Neville, 286
 Nies, 294
 Nigudkar, 377
 Nikolic, 375
 Noack, 404
 Noddack, 321, 391, 392
 Nordheim, 269
 Norrish, 84, 85, 108, 162, 216, 227, 228, 230, 233, 235, 237, 238, 271, 284, 286, 303, 305, 310, 323, 326, 342, 349, 353, 358
 Norton, 208, 361, 365
 Noyes, 152, 194, 195, 211, 227, 233, 234, 237, 259, 280, 282, 284, 328, 338, 339, 340

O

O'Bryan, 124
 Oda, 352

Ogg, 182, 185, 363
 Oldenberg, 53, 110, 174, 175, 220
 Olson, 249, 261, 269, 341, 345
 Onoda, 314
 Ordonneau, 401
 Orthmann, 44
 Orton, 261
 Ottmer, 131
 Overstreet, 419

P

Paal, 260
 Padelt, 169, 286
 Paneth, 119
 Parker, 147
 Parti, 209
 Patat, 84, 219, 227, 228, 264, 328, 345, 423
 Paul, 208, 364, 365
 Pauling, 349, 423
 Pearson, 174, 208, 227, 235, 236, 238, 264, 273
 Pease, 347
 Perez Vitoria, 239
 Perperot, 271
 Perret, 385
 Perrin, 56
 Peters, 336
 Phillips, 285
 Pick, 132
 Pickett, 201
 Pierce, 243
 Pitzer, 382
 Planck, 6
 Platz, 140
 Podashevskii, 132
 Pohl, 122, 123, 124, 129, 131, 132, 135, 136, 137, 140, 392
 Polak, 81, 301
 Polanyi, 96, 297, 424
 Polissar, 293
 Polley, 118
 Pool, 40, 268
 Popov, 87, 273
 Porret, 202, 203, 205, 336, 380
 Porter, C. W., 248, 261
 Porter, J. M., 169, 293, 362
 Potterill, 205
 Potts, 303, 305, 308, 313
 Povenz, 205
 Prasad, 377
 Predwotileff, 181
 Price, 84, 147, 171, 198, 202, 218, 224, 342, 348, 423
 Prileshajeva, 120, 235, 246
 Prilezajewa, 212
 Prince, 201
 Pringsheim, 44
 Prins, 407
 Pruckner, 262
 Purcell, 227, 235
 Purkis, 216, 217
 Pusenkin, 361

R

Rabinowitch, 46, 51, 81, 104, 269, 281, 282, 294, 313, 356, 357, 380
 Radley, 387
 Ram, 354
 Ramart-Lucas, 207, 223
 Ramsauer, 53
 Ramsperger, 215
 Randall, M., 114
 Randall, R. H., 40
 Rao, 246, 377
 Rathenau, 171, 353
 Ray, 213
 Reeve, 243
 Regener, 327
 Rehren, 281
 Reichert, 421
 Reincke, 350
 Renz, 386
 Rice, F. O., 4, 118, 119, 164, 175, 213, 215, 228, 283, 423
 Rice, K. K., 4, 213, 283
 Rice, O. K., 158, 344, 350
 Richardson, F. D., 170
 Richter, 379
 Rideal, 183
 Riding, 375
 Riechemeier, 102
 Riemann, 56
 Riggert, 352
 Ritchie, 104, 146, 297, 303, 305, 310
 Robinson, 102
 Rodebush, 110, 174, 271, 304
 Roe, 201
 Roelofsen, 404
 Rollefson, 42, 65, 70, 87, 115, 169, 187, 192, 225, 228, 286, 292, 303, 305, 306, 308, 309, 312, 313, 315, 316, 319, 320, 321, 322, 326, 336, 338, 354, 356
 Romeyn, 195, 282
 Rompe, 53
 Roof, 224, 354
 Roscoe, 308
 Rose, 196
 Rosen, 53, 78
 Rosenblum, 119, 351, 424
 Roseveare, 381
 Ross, 239
 Rossini, 165, 420
 Rothemund, 398
 Rothen, 222
 Roxburgh, 188
 Ruben, 413
 Rudberg, 360
 Rump, 363, 370
 Russell, 421
 Rydberg, 68

S

Sachsse, 102, 117, 183, 228, 229, 262, 276

- Saha, N. K., 205
 Salley, 271, 279
 Salmon-Legagneur, 207
 Saltmarsh, 233, 235, 238
 Samuel, 147, 209, 246
 Savard, 212
 Savost'yanova, 134
 Schaafsma, 267
 Scheibe, 198, 203, 205, 218, 221, 342, 369, 375, 396
 Schenk, 109, 140, 149, 276, 305
 Schifflett, 351
 Schlegel, 336
 Schlessinger, 107, 210
 Schmid, 157
 Schmidt, 289
 Schmitt, 361
 Schneider, E., 404
 Schneider, E. G., 124
 Schnetzler, 376
 Schnider, 247
 Schoming, 201
 Schon, 224
 Schönberg, 352
 Schou, 84, 223, 224
 Schryver, 401
 Schulze, 260
 Schumacher, 145, 146, 166, 167, 168, 170, 171, 273, 288, 293, 294, 319, 320, 333, 337, 362
 Schusterius, 376
 Schwab, 319
 Schwarz, 194, 391
 Scott, 262
 Semenoff, 312
 Sendai, 205
 Senftleben, 45, 64, 102, 268, 281
 Sen-Gupta, 147, 152, 164, 202, 205
 Sharma, 176
 Shaw, 217
 Sherman, A., 209, 240
 Sherman, J., 423
 Sherrill, 274
 Shljivic, 375
 Shorey, 401
 Shvartz, 177, 379
 Sickman, 119, 215, 228, 344, 350
 Silber, 261
 Simmons, 285
 Simon, 249, 260
 Simpson, 147
 Skrabal, 238
 Slotin, 176
 Smakula, 129, 136, 258
 Smallwood, 102
 Smekal, 130
 Smith, A. M., 405
 Smith, H. A., 271
 Smith, H. P., 338
 Smith, J. H. C., 224
 Smith, P. T., 348
 Smith, R. N., 226, 278, 360
 Smith, W. R., 248
 Snow, 222
 Solomon, 200
 Spence, 106, 111, 210, 228, 236
 Spinks, 169, 286, 293, 362, 363
 Spoehr, 397
 Sponer, 24, 46, 67, 86, 149, 156, 272, 421
 Spooner, 312
 Sprenger, 165
 Squire, 303, 305
 Stark, 2, 348
 Staud, 396
 Stauffer, 403
 Stavely, 118
 Steacie, 214, 217, 285
 Steele, 398
 Steigerwald, 229
 Stein, 173, 178, 180
 Steiner, 102, 104, 191, 196, 297, 394
 Stephan, 210
 Stern, 190, 391, 392, 402
 Stewart, H. R., 345
 Stewart, K., 194
 Stewart, T. D., 329
 Stieger, 167, 294, 314, 362
 St. Mrazek, 196
 Stobbe, 361
 Stock, 391
 Stoddart, 174
 Stoerner, 249, 260
 Stokes, 51
 Stoll, 401
 Stolle, 401
 Storch, 269, 271, 347
 Strutt, 42
 Stuart, 44, 250
 Stuckardt, 87
 Stücklen, 199, 200, 201
 Style, 176, 236, 379
- T**
- Talladin, 401
 Tammann, 134
 Tanasescu, 265
 Tate, 348
 Taube, 293, 362, 363
 Taylor, A. M., 141
 Taylor, H. A., 216
 Taylor, H. S., 84, 110, 119, 183, 184, 201, 240, 241, 271, 275, 276, 278, 279, 282, 283, 285, 342, 344, 346, 350, 379, 386, 423, 424
 Teller, 86, 149, 413, 419, 421
 Terenin, 65, 87, 120, 172, 181, 220, 235, 246
 Teves, 69, 78
 Thomas, 360
 Thompson, H. E., 341
 Thompson, H. W., 216, 217, 224, 233, 246, 354, 363, 366
 Tian, 173

Tiemeyer, 123
 Tietz, 326
 Tingey, 191
 Todd, 170
 Toporetz, 134
 Toul, 351
 Townend, 168, 362
 Treboux, 397
 Trenner, 84, 110, 423, 424
 Trivedi, 419
 Turner, 63, 64, 81

U

Unger, 303
 Urbach, 138, 391
 Urey, 164, 168, 175
 Urmston, 301

V

Vaidya, 258
 van der Beck, 327
 Van Niel, 397, 404
 Van Rysselberghe, 421
 van Tiggelen, 184
 Van Vleck, 209
 Vaughan, 328
 Verhoek, 160
 Vernon, 347
 Vesper, 292, 322
 Vogels, 375
 Volbert, 375
 Volman, 229, 354
 Volmer, 190, 352
 von Elbe, 177, 271
 von Halban, 375, 376
 von Hippel, 126, 129
 Vyeseige, 405

W

Wachholtz, 289
 Wagner, C., 316
 Wagner, H., 386
 Wagner, J., 238
 Wahl, 174
 Walker, M. K., 199
 Walker, O. J., 205, 245, 247
 Wallace, 167
 Walter, 199, 201
 Walters, 382
 Wansbrough-Jones, 241, 363, 374
 Warburg, 3, 60, 91, 145, 185, 190, 258, 327, 363, 370, 375, 400, 403, 405
 Wassiljewa, 189
 Watson, 147
 Watts, 262
 Wawilow, 56
 Webb, 40

Weber, 57, 181
 Weegman, 149
 Wegscheider, 262
 Weidenbaum, 329
 Weigert, 141, 262, 286, 307, 308, 327, 352, 353
 Weil, 392
 Weiss, 380, 421
 Weith, 341
 Welge, 183
 Wende, 110, 174, 271
 Wenner, 184
 West, H. L., 321
 West, W., 57, 107, 117, 201, 208, 210, 313, 364, 365
 Wieland, 149
 Wien, 39
 Wigand, 354
 Wiig, 91, 182, 183, 185, 211, 293, 294, 334
 Wilbur, 261
 Wild, G. L. E., 245, 247
 Wild, W., 108, 228, 236
 Wildermann, 313
 Willard, 331
 Willi, 247
 Williams, I., 341
 Williamson, 271
 Willstätter, 401
 Wilson, 382
 Windsor, 170
 Winkle, 237
 Winn, 382
 Winter, 91, 105, 302, 303
 Winther, 381, 385
 Wohl, 409
 Wolf, 222, 223, 366, 403
 Wolff, 320
 Wood, R. W., 4, 41, 43, 46, 51, 90, 103, 200, 269, 271, 383, 405
 Wood, W. C., 52, 81, 294
 Wulf, 144, 158, 164, 327
 Wulff, 138
 Wurmser, 176, 223, 379

Y

Yakovleva, 144, 145
 Yost, 322
 Young, K. W., 382
 Young, W. G., 224, 354

Z

Zemansky, 44, 274
 Zimmer, 262
 Zimmermann, 229
 Zipfel, 386
 Zoher, 384
 Zscheile, 398, 399

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